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U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP676

Part of Bureau of Standards Journal of Research, vol. 12, May 1934

FREEZING POINT OF RHODIUM

By Wm. F. Roeser and H. T. Wensel

ABSTRACT

The freezing point of rhodium was determined by measuring with a disappearing filament type of optical pyrometer the ratio of brightness of black bodies immersed in freezing gold and freezing rhodium. The rhodium was melted and frozen in vacuo to prevent the absorption of gases during melting. Attempts to operate with the rhodium in atmospheres of air and of nitrogen were not successful.

The ratio of brightness of black bodies at the freezing points of gold and rhodium was found to be 751 for wave length 0.6527 μ. This gives 1,966 degrees centigrade for the temperature of freezing rhodium when the gold point is fixed at 1,063.0 C and C_2 at 1.432 cm-degrees. The value 1,966 degrees centigrade is probably accurate to $\pm 3°$ C.

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I. INTRODUCTION

The development of a practical form of hollow inclosure or black body immersed in freezing platinum [1] and the demonstration that the radiation from this form of black body is sufficiently constant and reproducible to serve as a standard of light, immediately suggested the possibility of employing metals with higher melting points for this and similar purposes. The metals of the platinum group appear to be the most suitable for this purpose. The investigation of black bodies immersed in freezing rhodium and iridium was made primarily to determine the advantages and disadvantages of these metals for establishing standards of luminous intensity.

One application of this form of immersed black body has been the establishment of a scale of color temperature. This work, described elsewhere [2] in this Journal, required an accurate knowledge of the freezing points of at least three metals. The three selected, platinum, rhodium, and iridium, melt at temperatures which are well spaced on the scale of chromaticity.

II. PREVIOUS WORK

Previous observations on the melting point of rhodium are summarized and reduced to the International Temperature Scale [3] in table 1. In two cases, the apparent or brightness temperature of the

[1] B.S.Jour. Research, vol. 6, p. 1103, 1931.
[2] B.S.Jour. of Research, vol. 12 (RP 677), p. 527, 1934.
[3] Proc. 7th Gen. Conf. Weights and Measures, p. 56, 1927; Text in annex 4, p. 94; B.S.Jour. Research, vol. 1, p. 635, 1928.

metal at its melting point was reported. In deriving values for the true temperature from these, the value 0.29, reported by Henning [4] and also by Burgess and Waltenberg,[5] was used for the emissivity. All of the previous determinations were made by methods differing either in principle or detail and little can be said regarding their relative accuracy with the exception that Henning and Heuse improved upon the method used by Holborn and Henning and obtained a value approximately 70° C higher. The tentative value reported by Swanger was preliminary to the present work.

TABLE 1.—*Summary of determinations of the melting point of rhodium by various observers*

Observer	Year	Scale used			Reported values			True temperature on International Temperature Scale
		Au point	Pt point	C_2	Temperature		Wavelength	
					Apparent	True		
		°C	°C		°C	°C	μ	°C
Holborn and Henning [1]	1905	1,064		1.45	1,650		0.643	1,891
Mendenhall and Ingersoll [2]	1907	1,065	1,745 1,789			1,907 1,968		1,946
Von Wartenberg [3]	1910		1,745	1.46		1,940		1,960
Burgess [4]	1916	1,063		1.445		1,960		1,974
Henning and Heuse [5]	1924	1,063		1.43	1,720		0.622	1,958
Swanger [6]	1929	1,063		1.432		1,984		1,984
Present work	1933	1,063		1.432		1,966		1,966

[1] Preuss. Akad. Wiss. Berlin, Sitz. Ber., vol. 12, p. 311, 1905.
[2] Phys. Rev., vol. 25, p. 1, 1907.
[3] Verh. Deut. Phys. Gesell., vol. 12, p. 121, 1910.
[4] Jour. Frank. Inst., vol. 182, p. 19, 1916.
[5] Zeits. f. Physik., vol. 29, p. 157, 1924.
[6] B.S.Jour. Research, vol. 3, p. 1029, 1929.

In all of these determinations, with the exception of the two reported by Von Wartenberg and by Swanger, an optical pyrometer was sighted either on samples of rhodium heated electrically in air or on small bits of the metal placed on electrically heated materials. Von Wartenberg melted small samples of rhodium in a tungsten tube in vacuo. In the work reported by Swanger 5 to 10 cm^3 of the metal was heated in vacuo in a high-frequency induction furnace and an optical pyrometer was sighted either into a hole drilled into the metal or into an immersed sight tube similar to that used in the present work.

III. PRESENT WORK

In view of the applications to be made of the freezing point of rhodium, it was considered advisable to use the black body under exactly the same conditions for the temperature measurements, the brightness measurements, and the color comparisons. The last two require the use of a lens to form a magnified image of the opening in the black body, and the small size of this opening required that the distance between it and the lens should not exceed 17 cm to secure sufficient magnification to fill the field of the photometers available. This, of course, limits the distance between the observation window and the rhodium if the metal is to be melted in an atmosphere other than air.

One of the sources of error in the determination of the brightness of a black body by the method described in the paper on the Waidner-

[4] Zeits. f. Instrumentenkunde, vol. 30, p. 61, 1910.
[5] B.S. Bulletin vol. 11 (SP242), p. 591, 1915.

Burgess Standard of Light,[6] arises from the uncertainty in the value of the transmission of the lens and prism. The use of a black body immersed in freezing rhodium in an atmosphere other than air, requires the determination of the transmission of a window (which could seldom be kept entirely free from a film) in addition to that of the lens and prism. The film could have been avoided by using a longer tube as described by Swanger but it would not have been possible to make brightness measurements or color temperature comparisons under these conditions. In order to avoid the additional uncertainty due to the film on the window, a futile attempt was made to operate with the rhodium in air. It was known in advance that rhodium when melted in air absorbs gas which, during freezing, is released rather violently with the formation of "sprouts." The rhodium was mounted in a thorium oxide crucible in the same manner as in the case of platinum[7] and iridium.[8] In spite of the fact that the cover was tightly sealed on the crucible and that the metal was maintained above its melting point for only a few minutes, it sprouted severely, breaking the sight tube on the second freeze. Some of the sprouts through the cracks in the crucible extended as far as 2 cm into the insulation.

Attention was then directed toward operating with the rhodium in vacuo. The metal and crucible[9] were packed in a porcelain container which fitted into a pyrex tube about 7 cm in diameter. The pyrex tube was about 25 cm long and was provided with a tube for evacuating. The opening in the black body was about 16 cm from the pyrex window used in sealing the tube. Considerable difficulty was experienced with the film collecting on the inside of the window. Chemical and optical tests made to identify the material collecting on the window indicated that it was thorium oxide. In the first experiments the film collected on the window at a rate which produced a drift of about 1° C per freeze. In later experiments 3 diaphragms were placed between the window and the rhodium packed in the thorium oxide. The metal was maintained at a temperature just below its melting point for a total of 12 hours before making observations. After the window was cleaned the observation showed a drift of about 0.1° C per freeze. Examples of groups of observations with a large and a small drift are given in figure 1. In other experiments a fused silica window was placed inside the evacuated tube and connected to an iron rod in a side tube, so that the window could be placed over the opening in one of the diaphragms by means of a magnet during melting and moved aside during freezing. The observations then indicated a drift of about 0.3° C per freeze. The difference between the amount of film collected on the window in these experiments and in the preceding set of experiments is probably due to the fact that the insulation was not heated for an appreciable length of time before taking the observations.

In some of the above experiments, the effect of the final film on the window was also determined by measuring the transmission (for red light) of the window before and after a series of observations at the rhodium point. The change in the transmission of the window obtained in this way agreed with that indicated by the drift in the

[6] B.S.Jour. Research, vol. 6, p. 1103, 1931.
[7] B.S.Jour. Research, vol. 6, p. 1119, 1931.
[8] B.S.Jour. Research, vol. 10, p. 809, 1933.
[9] Acknowledgment is made to F. R. Caldwell who prepared the crucibles and black bodies and assisted in the observations.

observations. The pressure during the observations was between 0.001 and 0.05 mm of Hg. A liquid-air trap was placed between the diffusion pump and the tube containing the rhodium to prevent mercury vapor from diffusing back into this tube.

An attempt to melt and freeze the rhodium in an atmosphere of nitrogen was not successful. The sight tube broke during the second freeze. The film collected on the window in this case at about the same rate as in vacuo and it therefore was concluded that little could

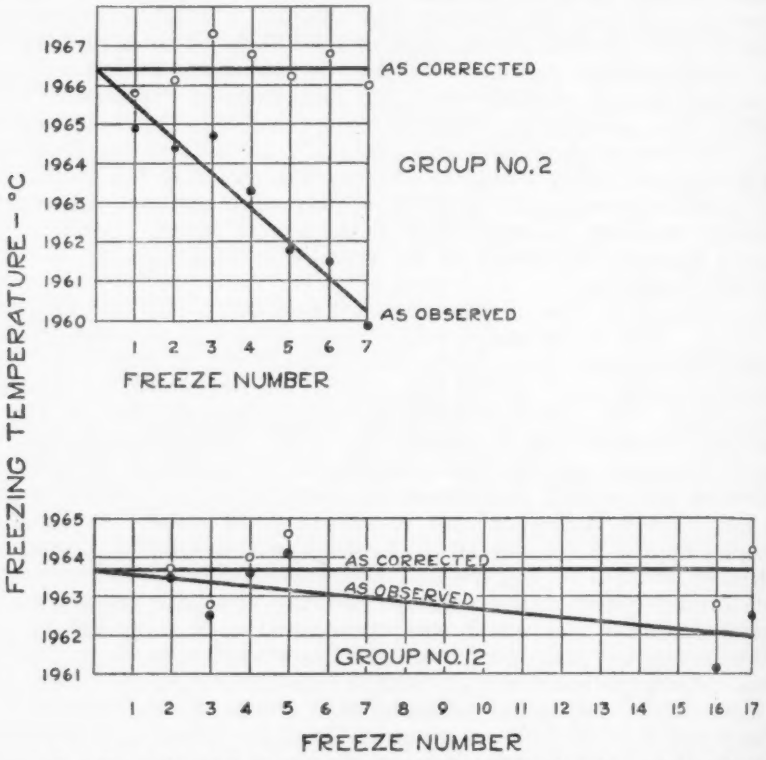

FIGURE 1.—*Examples of the drift in the observations at the freezing point of rhodium due to film collecting on the window.*

be gained by operating with the rhodium in an atmosphere of nitrogen.

The method of observation and the pyrometer were essentially the same as those used in determining the freezing points of platinum and iridium. Since the ratio of brightness of black bodies at the gold and rhodium points is approximately 750 for red light, a sector disk with less than 30 minutes of arc opening would be required if the ratio were to be measured in one step. Inasmuch as an opening of this size could not be measured with sufficient accuracy, the ratio of brightness was measured in two steps using two different combinations of sector disks. In each case, a black body was operated at a temperature between the freezing points of gold and rhodium. The intermediate temperature was 1,220 C in one case and 1,360 C in the other. The ratio of brightness of black bodies at the platinum and rhodium points was also measured. This ratio of brightness is

approximately 2.5, which requires a sector disk with about 40 percent transmission.

Observations at the freezing points of platinum and gold taken before and after the observations at the rhodium point showed no change in the pyrometer lamp during the course of this work.

The mean effective wave length of the red glass filter for the individual observers participating in this work was determined from the comparisons reported in the paper on "The Freezing Point of Iridium." The temperatures were calculated as described in the paper on "The Freezing Point of Platinum", with the exception that it was necessary to correct for the film collecting on the window.

In those cases in which a number of freezes were taken and the drift in the observations indicated that the correction was directly proportional to the number of freezes, correction was made on that basis. In other cases where only one or two freezes were taken and it was not possible to establish a drift in the observation, the change in the transmission of the window (for red light) was used to determine the correction to be applied.

IV. RESULTS

The calculated results are given in table 2. With the exceptions of groups 7, 11, and 13, the window was cleaned before each group of observations: After the observations in group 4, six freezes were used for another purpose and then the observations in group 11 were taken; all the observations in group 7 were taken between the 4th and 5th observation given in group 12; the observations in group 13 immediately followed those in group 9.

The ratio of brightness of black bodies at the freezing points of gold and rhodium was found to be 751 at wave length 0.6527μ from which the temperature of freezing rhodium was calculated as 1,966 degrees centigrade on the international temperature scale. At the same wave length the ratio of brightness of black bodies at the freezing points of platinum and rhodium was found to be 2.52. This ratio is consistent with the values 1,773.2 and 1,966 degrees centigrade for the freezing points of platinum and rhodium, respectively, to within about 0.3° C.

It is estimated that the error in the final result due to uncertainty in the transmission of the sector disks, effective wave length, photometric matching, departure from black body conditions and impurities in the metal, does not exceed 2.5° C if all are given the maximum value and if all are of the same sign. Uncertainty in any of the first three sources may cause the final result to be either high or low whereas that due to the departure from black body conditions would result in a low value for the freezing point.

The difference (1.7° C) between the mean of groups 3 to 10 and that of groups 11 to 13 would seem to indicate that the uncertainty in the measurement of the transmission of the sector disks is greater than that estimated. However, part of this difference may be due to the uncertainty in the correction applied for film on the window. Most of the observations in groups 11 to 13 were taken after some of those in groups 3 to 10, and required the application of larger corrections because the window was not cleaned in the meantime. The results do not show any systematic error in the method used in

applying the correction for the film. The final result, 1,966 degrees Centigrade for the freezing temperature of rhodium is probably accurate to ±3° C.

TABLE 2.—*Summary of observations at the freezing point of rhodium*

Group number	Base point	Temperature of intermediate black body	Atmosphere	Freezing point of Rh				Average correction applied for film
				Observer			Mean	
				HTW	WFR	FRC		
	°C	°C		°C	°C	°C	°C	°C
1	Fp of Pt (1,773.2)		Air	1,965.3			1,965.3	0
2	do		Vacuum	1,965.8				
						1,966.1		
					1,967.3			
				1,966.8				
						1,966.2		
					1,966.8			
				1,966.0			1,966.4	3.5
3	Fp of Au (1,063.0)	1,360	do	1,966.6				
					1,967.2			
				1,967.2			1,967.0	2.6
4	do	1,360	do			1,966.3		
					1,967.6			
				1,967.1			1,967.0	2.7
5	do	1,360	do	1,965.9			1,965.9	0
6	do	1,360	do	1,965.4				
					1,967.8			
						1,966.5	1,966.6	2.9
7	do	1,360	do	1,965.8				
				1,965.7				
					1,964.0			
						1,965.8		
				1,966.2				
					1,966.3			
						1,965.8	1,965.7	0.8
8	do	1,360	do	1,965.3				
					1,967.0		1,966.2	1.0
9	do	1,360	do	1,965.4				
						1,964.9		
					1,965.5			
						1,963.6	1,964.8	1.4
10	do	1,360	Nitrogen		1,965.9		1,965.9	1.8
11	do	1,220	Vacuum			1,964.8		
					1,966.6			
				1,967.6			1,966.3	16.9
12	do	1,220	do			1,963.7		
					1,962.8			
						1,964.0		
					1,964.6			
				1,962.8				
				1,964.2			1,963.7	0.8
13	do	1,220	do			1,962.5		
					1,963.4			
				1,964.3			1,963.4	2.7
Mean of groups nos. 1 and 2				1,966.0	1,967.0	1,966.2	1,966.3	
Mean of groups nos. 3 to 10				1,966.1	1,966.4	1,965.5	1,966.0	
Mean of groups nos. 11 to 13				1,964.7	1,964.4	1,963.8	1,964.3	
Weighted mean of all groups				1,965.7	1,965.9	1,965.0	1,965.6	

[FREEZING POINT OF RHODIUM, 1,966 DEGREES CENTIGRADE]

In view of the fact that the film collecting on the window produced an uncertainty in the determination of its light absorption, the black body at the freezing point of rhodium, as set up in this work, is not considered suitable for use as a standard of luminous intensity.

V. PREPARATION AND PURITY OF THE RHODIUM

By Edward Wichers

The rhodium used in this work was carefully purified [10] by a procedure which corresponded for the most part with that described by Wichers, Gilchrist, and Swanger.[11] Since the publication of that paper, further experience has shown that the repeated precipitation of ammonium rhodium nitrite, although very effective for removing other impurities, is not satisfactory for removing more than very small amounts of iridium. In order to reduce the iridium content of the rhodium to an amount suitable for the application of the nitrite process, the following method was used for effecting solution of the rhodium. The impure rhodium was mixed with about 20 parts of lead and the mixture fused in a graphite crucible at about 1,000 C for half an hour.[12] The resulting alloy was treated with nitric acid to dissolve most of the lead. In this treatment a little rhodium dissolves, but most of it is left as a finely divided alloy with lead. This alloy was vigorously attacked, first with concentrated hydrochloric acid, and then with aqua regia, leaving finally a residue which contained nearly all of the iridium, together with a small portion of the rhodium.

Most of the lead was precipitated from the acid solutions with sulphuric acid, added in slight excess. The filtrates from the lead sulphate were combined and evaporated to a small volume to expel most of the free acids and to obtain a second precipitate of lead sulphate. The filtrate from this precipitate was treated with a sufficient amount of a solution of sodium nitrite to neutralize the remaining free acid and to convert the rhodium chloride into sodium rhodium nitrite, $Na_3Rh(NO_2)_6$. The solution was boiled to complete the conversion to nitrite. To this solution, which contained about 50 g of rhodium per liter, was added about 30 g of sodium sulphide crystals for each 100 g of rhodium. This was done to precipitate certain base metal impurities, such as copper and lead. Some of the platinum metal impurities, especially palladium, are partially precipitated by this treatment, but very little of the rhodium is lost. After standing overnight, the sulphide precipitate was filtered off and the solution boiled to consume any remaining sodium sulphide by its reaction with platinum metal impurities or with the rhodium itself. After removing the second small precipitate of sulphides, the solution was cooled to about 15 C and treated with a solution of ammonium chloride to precipitate a salt which has generally been regarded as $(NH_4)_3Rh(NO_2)_6$ but which may be a mixed sodium and ammonium rhodium nitrite. About 200 g of NH_4Cl was used for each 100 g of rhodium. This proportion includes a small excess of ammonium chloride, which decreases the solubility of the double salt.

After filtering and washing the salt, it was decomposed with hydrochloric acid diluted with 3 or 4 volumes of water. The chloride solution was then evaporated to expel most of the hydrochloric acid and the cycle of operations with sodium nitrite, sodium sulphide, and ammonium chloride repeated six times. The quantity of sodium sulphide used was decreased each time, and the sulphide precipitates were examined chemically for lead. Lead was not detected after the

[10] By R. K. Bell.

[11] "Purification of the Six Platinum Metals", Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

[12] Although it might sometimes be disadvantageous to add lead to the rhodium, because of the difficulty of eliminating all of that metal in the subsequent process of purification, it is usually of no consequence, because lead is very often already present as an impurity in the rhodium.

fourth precipitation. At this stage a solution of sodium nitrite which had been treated to remove traces of base metals was substituted for the ordinary reagent.

Spectrographic examination of the rhodium from the fifth precipitation failed to disclose the presence of any other platinum metals, but indicated the presence of a trace of lead. Lead was not found in the metal from the sixth precipitation. The salt obtained by the seventh precipitation was converted into a chloride solution, by means of hydrochloric acid, and ammonium chloride was added in slight excess of the amount equivalent to $(NH_4)_3RhCl_6$. The double chloride was then precipitated, from this solution, containing about 100 g of rhodium per liter, by adding one and one half times its volume of 95 percent alcohol. The salt was washed with alcohol, dissolved in water, and reprecipitated by means of alcohol from a somewhat more dilute solution. The salt thus prepared contained, after drying, 30.7 percent of rhodium, which is about midway between the rhodium content of $(NH_4)_2RhCl_5$ and $(NH_4)_3RhCl_6$.

The salt was ignited in a porcelain container in a resistance furnace in such a way as to prevent contamination with metal vapors from the winding. The residue was reduced to rhodium sponge by ignition in hydrogen and the sponge digested with water to extract a small amount of alkali salts. The sponge was then compressed into pellets in a steel mold and melted in a thorium oxide crucible, in vacuo, to form an ingot of the proper shape and size.

The chemicals used in the purification were all of analytical reagent quality, except that some of the sodium nitrite used was specially treated to remove base metals, as previously mentioned. A more detailed discussion of the process of purification is given in the reference cited.[13]

After the work on the determination of the melting point had been completed a portion of the ingot was prepared for spectrographic examination and another for determination of the electrical resistivity and the temperature coefficient of resistance.[14] The latter specimen was obtained by sawing a quarter segment out of the ingot and work-it into wire by the method described by Swanger.[15]

The resistivity was 4.3 microhm-cm at 0 C, and the ratio $\frac{R_{100}-R_o}{100R_o}$ was 0.00457. The former value is lower, and the latter higher, than any corresponding value found in the literature, thus indicating that this rhodium had a higher degree of purity than any whose electrical properties have been reported heretofore. Spectrographic examination [16] gave no evidence that the rhodium had taken up thorium from the refractory crucible or had been otherwise contaminated during the experimental work, except perhaps by a trace of iron, presumably introduced during the forging of the metal or the drilling of the ingot for the sight tube, in spite of the fact that the ingot was digested with boiling hydrochloric acid after each such treatment. It is believed that the total metallic impurities in the rhodium, at the completion of the work, did not exceed 0.01 percent, and may have been considerably less.

WASHINGTON, March 1, 1934.

[13] See footnote 11.
[14] Both determinations made by Wm. F. Roeser.
[15] Melting, Mechanical Working, and Some Physical Properties of Rhodium, B. S. Journal Research, vol. 3, p. 1029, 1929. The specimen was prepared by J. G. Thompson.
[16] By B. F. Scribner.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP677

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ESTABLISHMENT OF A SCALE OF COLOR TEMPERATURE

By H. T. Wensel, D. B. Judd, and Wm. F. Roeser

ABSTRACT

A number of 400-watt projection lamps were color matched with black bodies immersed in freezing platinum, rhodium, and iridium. From these lamps working standards of color temperature were prepared, interpolation between the three fundamental points being accomplished by making use of the systematic difference between the color temperature of the lamp and the brightness temperature of the inside of a particular turn of the coiled tungsten filament.

These working standards embody a reproducible scale of color temperature which is consistent with the International Temperature Scale within 5° K everywhere in the range from 2,000 to 2,800 K.

The new scale assigns higher values to any given source than the scale previously used at the Bureau of Standards and which was supposed to be the same as the Nela scale of color temperature. The differences are 22° K at the platinum point and 14° K at the rhodium and the iridium points.

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I. INTRODUCTION

The International Commission on Illumination at its 1931 meeting in Cambridge [1] adopted, among other things, a recommendation for standard illuminants, which has been translated as follows, "It is recommended that the following three illuminants be adopted as standards for the general colorimetry of materials:

A. A gas-filled lamp of color temperature 2,848° K.

B. The same lamp used in combination with a filter composed of a layer one centimeter thick of each of two solutions, B_1 and B_2, etc.

C. The same lamp used in combination with . . . . . two solutions, C_1 and C_2, etc."

The ability of an experimenter to set up any one of these recommended standard illuminants depends on his ability to operate a gas-filled tungsten lamp at 2,848 K color temperature. No statement was

[1] Proceedings of the 8th session, Commission Internationale de l'Élairage, Cambridge, Sept. 1931, p. 19.

made, however, as to how the lamp should be brought to this color temperature nor what existing color temperature scales, if any, should be accepted as authoritative. A feeling apparently existed among the representatives from the several countries that the realization of the standard illuminants was uncertain in this respect because informal arrangements were made at the time for an intercomparison of the color temperature scales then in use in England, Germany, France, and the United States.

The temperature [2] of a hollow enclosure or black body which color matches a given illuminant is called the color temperature of that illuminant. In accord with this definition, the direct visual comparison of such an illuminant with a black body of known or measurable temperature is probably the most certain method of determining its color temperature. This method has presumably been used in the establishment of the various scales in use except for the higher temperatures. At the higher temperatures, it is difficult to control the temperature of black bodies and therefore the method of visual comparison has been supplemented by indirect methods involving a calculation of the color temperature from the measured spectral energy distribution. In one of these, called the red-blue ratio method, the color temperature of an illuminant is taken to be that of a black body which radiates at two selected wave lengths in the same ratio as the illuminant in question. In another method the temperature of that black body is selected whose spectral energy distribution throughout the visible spectrum, most nearly "fits" that of the illuminant. Several criteria, each yielding a slightly different result and none satisfactory from a theoretical standpoint, are available for thus selecting the black body which will presumably give the best color match.

II. SCALES NOW IN USE

There are almost no data available on the agreement among the scales used in different countries nor on the basis for any of these scales except the one used in the United States. In this country the scale universally used is the one established and maintained by the Nela Research Laboratory.

The high-temperature scale used at that laboratory was based on Wien's law of radiation using 1,828 K for the palladium point and 1.435 cm degrees for the second constant in the radiation formula. The Nela color temperature scale was established up to about 2,600 K by direct comparison with a black body in the form of a carbon tube furnace. From correspondence with the Nela laboratory we understand that the scale was then extended up to 3,000 K by indirect methods and considerably less confidence was therefore placed in this portion of the scale.

The scale in use at the Bureau of Standards since 1922 was based on 3 lamps obtained from and calibrated by the Nela laboratory, 2 in 1920 and 1 in 1922. Of these the first was calibrated at 2,360 K, the second throughout the range 1,719 to 2,448 K, and the third throughout the range 2,334 to 2,820 K. Meanwhile the spectral energy distribution of a 500-watt stereopticon lamp, designated as

[2] Expressed in this work on the International Scale. This temperature scale was adopted in 1927 by 31 nations and is in almost universal use. On this scale the freezing point of gold is defined as 1,063 C and the value of C_2 is taken as 1.432 cm deg.

B.S. no. 1,717, had been determined radiometrically [3] at a particular voltage and used to deduce a color temperature [4] of 2,848 K. Another lamp, which had been color matched against B.S. no. 1,717, was then sent to the Nela laboratory and compared with their standard. The average of four determinations [5] was given as 2,848 K. The exactness of this agreement was apparently accidental and has created the impression that this point on the scale was determined with far more accuracy than was actually the case.

All three of the lamps received from the Nela laboratory had thus been calibrated at 2,360 K and comparisons indicated that they agreed at this point to about 5° K. Slight adjustments in the assigned voltages were accordingly made to make them agree exactly. The situation was not so fortunate at the 2,848 point. The Bureau had only one lamp calibrated by the Nela laboratory at this point. It was found that this lamp (a duplicate of B.S. 1,717) operated to reproduce the 2,848 point color matched approximately the lamp calibrated from 2,334 to 2,820 K when operated to reproduce 2,820 K, although the latter lamp is too purple to match exactly the 2,848 lamp at any voltage. The scale largely used at the Bureau since 1922 has been based on the 2,848 K point as embodied in lamp B.S. 1,717 and on the Nela 2,360 K point, interpolation being made by means of the rotatory dispersion colorimeter.[6] In 1932 another duplicate of B.S. 1,717 was sent to the lamp-development laboratory at Nela Park and a check to 2° K obtained at 2,848 K.

III. PRESENT WORK

1. BASIS OF THE PRESENT SCALE

The purpose of the present work is to establish a scale of color temperature based upon thermometric fixed points, by color matching a number of incandescent lamps with hollow enclosures immersed in freezing metals. For this purpose the following three metals are available whose freezing points have been accurately determined and are spaced at suitable intervals:

1. Platinum, freezing point [7] ---------- 2046±1° K
2. Rhodium, freezing point [8] ---------- 2239±3° K
3. Iridium, freezing point [9] ---------- 2727±3° K

One obvious advantage of the scale established on this basis is the means available for checking the lamp standards at the three fixed points at any time this may be deemed necessary. Moreover, in working with the invariable light sources provided by hollow enclosures immersed in freezing metals the accuracy attainable is of a higher order than has been attained by other methods.

2. OPTICAL ARRANGEMENTS

The colorimetric comparisons were made with a Lummer-Brodhun photometer head from which the contrast strips had been removed. The field is the familiar double-trapezoid type, 9° wide by 13° high.

[3] For complete details see B.S. Scientific Papers, vol. 18, p. 221, 1922-23.
[4] Quite apart from the uncertainty of the radiometric measurements, the uncertainty in this deduced value may be judged from the fact that Priest (B.S. Scientific Papers, vol. 17, p. 231, 1921) at first deduced 2,830 K from the same data and that the method of Davis (B.S. Jour. Research, vol. 7, p. 671, 1931) yields 2,860 K.
[5] Reported Aug. 11, 1921.
[6] I. G. Priest, B.S. Scientific Papers, vol. 18, p. 221, 1922.
[7] Roeser, Caldwell, Wensel, B.S. Jour. Research, vol. 6, p. 1119, 1931.
[8] Roeser and Wensel, B.S. Jour. Research, vol. 12, p. 519, 1934.
[9] Henning and Wensel, B.S. Jour. Research, vol. 10, p. 809, 1933.

The substitution method was used. The photometer field was illuminated in essentially the same manner as described in the work [10] on the Waidner-Burgess Standard of Light, one side of the photometer head being illuminated either with light from the black body or with light from the standard lamp. The other side of the photometer head was illuminated by light from a comparison lamp.

It does not appear possible to dispense with the lens between the black body and the photometer. Without a lens, the illumination is much too low for accurate measurements. Moreover, this illumination coming partly from the opening in the black body and partly from the regions around this opening would be considerably redder than the light from the opening which is characteristic of the fixed point. The lens, however, images these colder parts outside the photometric field so that only light from the opening itself enters the photometer. The relative aperture of the lenses used was f/11 in each case. Inasmuch as a lens must be used, the use of a prism adds no further difficulty since the chromatic effect of the combination can be determined as readily as that of a lens alone.

Several prisms and about a dozen lenses were examined without finding a combination sufficiently free from selectivity to yield a good color match. All were slightly greenish. Since, as will appear later, the black body was an exact color match for the standard lamps when burned at the proper voltage, the latter did not yield a color match at any voltage with the black body viewed through the lens and prism. The chromatic effect of the lens and prism could be eliminated by placing them in front of the standard lamps as well. This, however, would require frequent time-consuming realinements of the optical parts and was found to be unnecessary since a piece of ordinary window glass of suitable thickness placed before the standard lamp permitted a color match with the black bodies as seen through the lens and prism. Evidently a "green" comparison lamp was required and this was obtained by a filter made of two opposing wedges of window glass placed in front of the comparison lamp. This filter is not very selective; the thickness of wedge required for one lens-prism combination transmits only 7 percent more in the middle of the spectrum than at the ends. The other combination requires a filter selective by only 4 percent. As will appear later, the two lens-prism combinations gave essentially identical results.

The greenish wedge in front of the comparison lamp has the same effect as a comparison lamp with a greenish globe and (as long as we are able to secure a color match) does not concern us further. The wedge setting was not changed during any set of measurements. Since both the black body viewed through the lens and prism and the standard lamps viewed through the selected piece of window glass matched the "green" comparison lamp, it follows that the black body and the standard lamps both viewed directly can be color matched if the selective effect of the piece of window glass is the same as that of the lens and prism. This equality was established for two lens-prism combinations experimentally.

A tungsten lamp was color matched against the "green" comparison lamp, first with the lens and prism interposed and then with the piece of window glass interposed. In each case the color match was perfect but a very small voltage difference was observed in the two settings,

[10] Wensel, Roeser, Barbrow, and Caldwell, B.S. Jour. Research, vol. 6, p. 1103, 1931.

indicating that the equivalence between the piece of window glass and the lens-prism combination was not exact.

These voltage differences, equivalent to differences in color temperature as shown in columns 2 and 4 of table 1, were applied to the results obtained in the main body of the work. An independent check on these corrections was made by measuring separately the effect of the window glass and each of the two lens-prism combinations. In these measurements the slight green difference had to be tolerated; hence the accuracy of the corrections obtained by subtraction (columns 3 and 5) was relatively low. However they were found to equal, within experimental error, the corrections measured directly by interchanging the two devices. Another check on these corrections was obtained by using both lens-prism combinations in the actual work and noting the agreement obtained in the two cases after the corresponding corrections had been applied.

TABLE 1.—*Corrections to be applied when using window glass to compensate for lens-prism combination*

Temperature of source	Correction when using lens no. 1		Correction when using lens no. 2	
	By direct measurement	By subtraction	By direct measurement	By subtraction
°K	°K	°K	°K	°K
2,046	0	0	−5	−2
2,239	0	−2	Not used	Not used
2,727	0	+4	−6	−7

3. STANDARD LAMPS

An extensive study has been made of the aging characteristics of several types of available lamps.[11] As a result the type selected for this work was a 400-watt mogul base projection lamp having a coiled monoplane filament in a tubular bulb. At 110 volts these lamps operate at a color temperature of 3,100 K where they have a total life of only 50 hours. At 2,727 K however, their qualities are remarkably constant, the color temperature (after the initial half hour) decreasing at the rate of only 0.03° K per hour of use.

4. FREEZING METALS

The technique employed in melting and freezing the three metals is exactly the same as that used in the freezing point determinations and the work on the Waidner-Burgess Standard of Light. In the case of rhodium, which must be melted in vacuo and observations therefore made through a furnace window, two pyrex windows were used, one on the evacuated tube containing the crucible and the other placed in front of the standard lamps. An interchange of these two windows, when color matching two lamps, showed that no difference between them could be detected. In this work the technique developed in the freezing point determinations made it possible to avoid trouble from film collecting on the window used to seal

[11] D. B. Judd, Jour. Opt. Soc. Am., vol. 23, p. 118, 1933.

the tube containing the rhodium. After a series of observations at the rhodium point the window was removed and observations made on a tungsten lamp first through P_1 (the window used on the furnace) and then through P_2, the compensating plate. The voltage of the lamp observed alternately through these was maintained constant and the values in table 2 are settings on the comparison lamp to produce a color match. Table 2 shows also the precision attainable in color matching with a Lummer-Brodhun contrast photometer.

TABLE 2.—*Test showing absence of error due to film on pyrex plate P_1*

[Lamp voltage 44.0 v]

	Observations through—				
	P_1	P_2	P_1	P_2	P_1
	v	*v*	*v*	*v*	*v*
Settings on voltage of comparison lamp to produce color match	42.1	42.2	42.2	41.9	42.0
	41.9	42.2	42.0	41.8	42.2
	41.8	41.9	42.0	41.8	42.0
	42.1	42.2	41.9	41.9	42.2
	42.2	42.0	42.2	41.8	42.0
	42.2	42.2	42.1	42.1	41.9
Mean	42.05	42.12	42.07	41.88	42.05

	Volts
Mean of observations through P_1	42.06
Mean of observations through P_2	42.00

0.06 volt equivalent to 1.2° K.

5. RESULTS

Three groups of three lamps each were color matched with the black bodies, one group at each of the thermometric fixed points. In making observations each observer made 6 settings on 1 lamp, 6 settings on the black body, 6 settings on a second lamp, 6 additional settings on the black body, and finally 6 settings on the third lamp. Observer KSG was available only part of the time and did not make observations when lens no. 2 was employed. Observations with the second lens-prism combination were not made at the rhodium point but the results at the other two points establish the fact that the same result is obtained with each lens. The results of the comparisons are given in tables 3, 4, and 5.

TABLE 3.—*Voltage on lamps to match black body at the platinum point (2,046 K)*

[A change of 1 volt produces a change of 20° K]

Observer	Lens used	Lamp		
		8650	8651	8935
	Number	*Volts*	*Volts*	*Volts*
HTW	1	34.74	34.74	33.93
	1	34.58	34.51	33.60
	2	34.80	34.90	33.69
DBJ	1	34.84	34.80	33.94
	1	34.62	34.59	33.81
	2	34.65	34.53	33.82
WFR	1	34.53	34.51	33.57
	1	34.70	34.59	33.83
	2	34.55	34.61	33.39
KSG	1	34.68	34.49	33.80
Mean with lens no. 1		34.67	34.60	33.78
Mean with lens no. 2		34.67	34.68	33.63
Mean of all observations		34.67	34.63	33.74

TABLE 4.—*Voltage on lamps to match black body at the rhodium point (2,239 K)*

[A change of 1 volt produces a change of 17° K]

Observer	Lens used	Lamp		
		9023	9024	9025
	Number	*Volts*	*Volts*	*Volts*
HTW	1	44.20	44.40	44.23
	1	44.20	44.40	44.24
DBJ	1	44.26	44.34	44.27
	1	44.23	44.36	44.23
WFR	1	44.28	44.30	44.23
	1	44.17	44.19	44.20
Mean		44.22	44.33	44.23

TABLE 5.—*Voltage on lamps to match black body at the iridium point (2,727 K)*

[A change of 1 volt produces a change of 14° K]

Observer	Lens used	Lamp		
		8934	8936	8937
	Number	*Volts*	*Volts*	*Volts*
HTW	1	75.51	75.23	75.24
	2	75.38	74.93	75.38
DBJ	1	75.56	75.14	75.33
	2	75.47	75.00	75.24
WFR	1	75.52	74.82	75.53
	2	75.56	75.02	75.24
KSG	1	75.55	74.85	75.50
Mean with lens no. 1		75.54	75.01	75.40
Mean with lens no. 2		75.47	74.98	75.29
Mean of all observations		75.51	75.00	75.35

The 3 points on the color-temperature scale, as embodied in the 9 lamps designated as reference standards, were then transferred to 3 working standards, each of these 3 lamps being calibrated in this way at all 3 points. In making the transfers, data were obtained on the differences between the three reference standards of each group. The three reference standards embodying the platinum point had a total spread of 1.9° K; the total spread at the rhodium and iridium points was 1.2 and 0.9° K, respectively. The precision of setting was lowest at the platinum point because the field brightness was low, and this probably accounts for the greater spread. The results indicate that the overall precision is very near the limit attainable in color temperature measurements.

6. INTERPOLATION BETWEEN FIXED POINTS

The extensive work done at the Nela Research Laboratory on the properties of tungsten has established the fact that a given change in brightness temperature corresponds to an approximately equal change in color temperature of a given specimen of tungsten. This offered a simple means of determining the color temperature of the 3 working standards at voltages between those at which these lamps match the 3 black bodies immersed in freezing metals.

The inside portions of a coiled tungsten filament approximate a black body and have a color temperature below that of the outside portions. The color temperature of the lamp as a whole is somewhere between. The turns near the ends of the coils are relatively cold, but they are few in number, radiate less, and do not have a marked effect upon the color temperature of the lamp.

Lamp 9022, one of the three working standards, was operated at 2,727 K color temperature and the coils were explored with an optical

pyrometer to locate the brightest turn. The brightness temperature ($T_{0.65}$) of the inside of this turn was found to be 2,662 K, while that of the outside was 2,486 K.[12] Thus the color temperature of the lamp is obtained, at this voltage, by adding 65° to the reading of the optical pyrometer when sighted upon the inside of this turn. Considerable variation was found from turn to turn in the brightness temperature, especially toward the ends of the coils. For *a particular turn*, however, the difference between the color temperature of the whole lamp and the brightness temperature inside the turn will obviously be a function of the voltage. For the brightest turn of lamp 9022, this difference was respectively 22°, 31°, and 65° K at the voltages corresponding to the 3 fixed points platinum, rhodium, and iridium, see

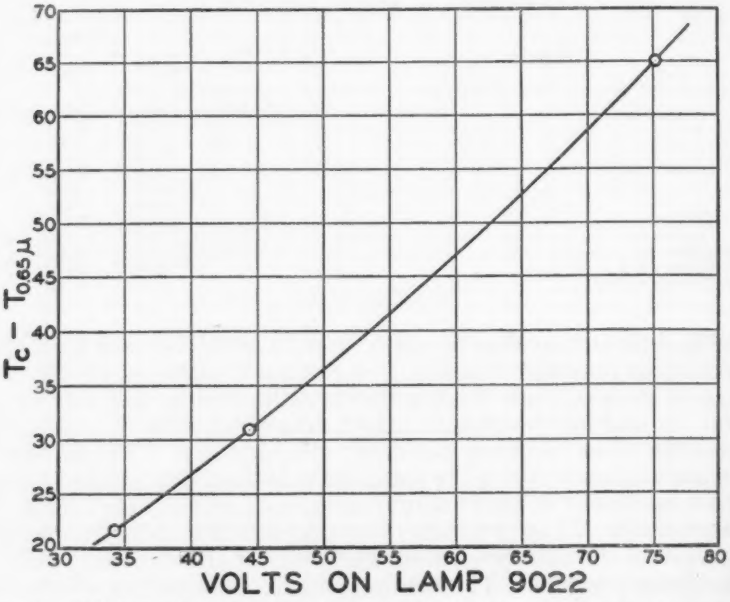

FIGURE 1.—*Difference between color temperature of lamp and apparent temperature of the inside of the brightest turn as a function of voltage.*

figure 1. By using this curve the color temperature for any voltage may be obtained from an optical pyrometer reading on the brightest turn which we may call A. This was done for six intermediate voltages. The entire process was then repeated using two other turns B and C of this same lamp, see table 6. The differences for these turns were greater than for A, being respectively 78° and 123° K at color temperature 2,727 K. The interpolated values of color temperature, as shown in table 6, may all be accurately represented by the formula,

$$T_c = 625 + 242.5\sqrt{V}$$

The values in table 6 have been given merely to demonstrate that the interpolated values do not depend upon the particular turn observed with the optical pyrometer. The results for the other two

[12] From this figure and the radiation characteristics of tungsten (Forsythe & Worthing, Astrophys. Jour. vol. 61, p. 146, 1925) the true temperature of this turn was calculated as 2,717 K and the color temperature of the outside portion as 2,785 K.

lamps may be expressed by similar relations. The formulas for the three lamps are as follows:

$$\text{Lamp 9020,} \quad T_c = 617 + 241.8\sqrt{V}$$
$$\text{Lamp 9021,} \quad T_c = 620 + 243.6\sqrt{V}$$
$$\text{Lamp 9022,} \quad T_c = 625 + 242.5\sqrt{V}$$

TABLE 6.—*Interpolated values of color temperature for lamp 9022*

Volts	Turn			Mean for 3 turns	By formula $T_c = a + b\sqrt{V}$
	A	B	C		
	°K	°K	°K	°K	°K
34.32	2,046	2,046	2,046	2,046	2,046
37.10	2,104	2,105	2,100	2,103	2,102
40.16	2,163	2,160	2,163	2,162	2,162
44.26	2,239	2,239	2,239	2,239	2,238
49.33	2,329	2,326	2,327	2,327	2,328
55.15	2,426	2,423	2,427	2,425	2,426
61.17	2,525	2,523	2,524	2,524	2,522
68.08	2,624	2,623	2,626	2,624	2,626
75.10	2,727	2,727	2,727	2,727	2,727

These equations are merely empirical relations which happen to be applicable to this particular type of lamp.

It may be noted that the scale can be extended both downward and upward (say to 2,848 K) either by these formulas or by reference to brightness temperature, or by suitable filters of known spectral transmission, such as the Davis-Gibson liquid filters. [13]

IV. DISCUSSION OF RESULTS

1. ANALYSIS OF ERRORS

In estimating the errors in the present scale as embodied in the 3 groups of reference standards it must be remembered that the temperatures of the immersed black bodies are known somewhat more accurately than the freezing points of the pure metals. For example, in assigning an uncertainty of 3° to the freezing point of iridium allowance was made for possible impurities in the metal used and for the fact that the black body enclosure may be at a slightly lower temperature than that of the metal in which it is immersed. The temperature of the black body itself which is all that matters in the present work, was determined with an uncertainty of less than 2°. This arises through uncertainty in measuring the angular aperture of the sector disk, through uncertainty in the effective wave length of the red filter and through the usual experimental uncertainty of photometric matching.

In table 7 is given the error analysis for the individual reference standards. Wherever possible the uncertainties are computed as 4.9 times the probable error; this product has sometimes been called the "huge error" because it is an error such that the chance of occurrence of an equal or greater error is only one in a thousand. In cases which do not permit such a computation, the uncertainty given approximates the huge error as closely as can be estimated. The uncertainty of

[13] B.S. Miscellaneous Pub. 114, 1931.

any individual working standard is slightly greater than the values given in table 7 because of the error introduced by the additional color matching, but it is estimated as nowhere greater than 5°.

TABLE 7.—*Analysis of errors for the individual reference standards*

Color temperature	2,046 K	2,239 K	2,727 K
	° *K*	° *K*	° *K*
Uncertainty in temperature of cavity	1.1	1.4	1.9
Experimental uncertainty of color matching	3.2	2.2	1.7
Uncertainty in lens-prism-compensator correction (table 1)	2.4	2.0	1.8
Total uncertainty (square root of the sum of the squares)	4.1	3.3	3.1

2. COMPARISON WITH PREVIOUS SCALES

The question of greatest interest to people who depend on measurements of color temperatures probably is, "How much does the present scale differ from previous scales?"

As stated in section II, the Bureau had one lamp calibrated by the Nela Research Laboratory from 1,719 to 2,448 K. When operated at the voltage certified to give 2,046 K, this lamp has a color temperature of 2,068 K on the present scale. When operated at the voltage giving 2,239 K on the Nela scale, it has a color temperature of 2,253 K.

The Bureau had a second lamp calibrated from 2,334 to 2,820 K by the Nela laboratory. When this lamp was operated to yield 2,727 K on the Nela scale, it would have to be assigned a value of about 2,775 K to agree with the present scale, but this lamp is too purple to color match the other lamps at any voltage.

The Bureau of Standards lamp certified by the Nela laboratory to yield 2,848 K can be operated to yield 2,727 K on the Nela scale by recourse to the relation between voltage and color temperature. When this is done its color temperature is 2,741 K.

The differences between the new scale and that previously maintained at the Bureau are summarized in table 8. It is not known however, how accurately these differences apply to the scale as maintained at Nela Park.

TABLE 8.—*Difference between present scale and previous scale*

Lamp	Color temperature		Difference
	On previous scale	On present scale	
	° *K*	° *K*	° *K*
A	2,046	2,068	22
	2,239	2,253	14
B	2,727	2,775	[1] 48
C	2,727	2,741	14

[1] The old Bureau scale was not based on this lamp.

Acknowledgment is made to K. S. Gibson who served as one of the observers in part of the work and who, together with D. B. Judd, made the transfers to the working standards and the comparisons with the Nela scale.

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U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

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A PROPELLER-VIBRATION INDICATOR

By Hugh L. Dryden and L. B. Tuckerman

ABSTRACT

It is believed that fatigue failures of aircraft propellers, which occasionally occur, are due to resonant vibrations of the propeller or the propeller-engine assembly. This paper describes an instrument to be mounted on the end of the engine shaft for determining the engine speeds at which dangerous vibrations occur. The instrument has been tested on the propeller vibration apparatus at the Bureau of Standards, and arrangements have been made for trying it on an airplane.

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I. INTRODUCTION

At the request of the Aeronautics Branch of the Department of Commerce the Bureau of Standards has been investigating the causes of failures of aircraft propellers, because these failures, though very few in number in comparison with the large number of propellers in service, generally cause serious and sometimes fatal accidents. All the propeller failures examined at the Bureau of Standards have, with a few exceptions, had the characteristics of fatigue failures, that is, failures due to vibratory stresses. Not only is this true, but the evidence seems to show that they are fatigue failures caused by relatively few alternations of relatively high stresses. The only phenomenon which has been found to be capable of producing the high stresses necessary to produce these failures is the phenomenon of resonant vibrations either of the propeller or of the combination of propeller and engine.

To study the stresses produced in such resonant vibrations, a propeller vibrating apparatus was constructed at the Bureau of Standards. This apparatus has been briefly described in BS. Research Paper 556. The work so far carried out on this apparatus indicates that large resonant vibrations occur only when the frequency of the exciting torque is within 1.0 cycle per second of one of the natural frequencies of the system. Even under flight conditions, it does not seem probable that large vibrations would exist at frequencies differing from one of the natural frequencies of the system by more than a few cycles per second.[1]

[1] We have measured the stress distribution in the principal modes of vibration for two propellers and have computed the stress distribution for one propeller. The measured and computed values were found to agree very well. This part of the investigation will be described in a subsequent paper.

If these conclusions are warranted, propeller failures in flight are in most cases to be ascribed to the occasional coincidence, over relatively short periods of time, of engine speed (or its multiples or submultiples) with a resonant frequency of the propeller or the propeller-engine assembly. Further, the most direct and immediate method of avoiding future propeller failures is (as has already been pointed out by the Army engineers)[2] never to fly even for a few seconds at any such critical engine speed.[3]

To make this method workable, some certain means must be available for determining these critical engine speeds, not merely for a given propeller or even a given combination of propeller and engine, but for a given combination of propeller and engine under actual flight conditions.

The War Department and the Bureau of Standards have experimented with nonrotating propeller and hub combinations. On the basis of certain theoretical investigations it is possible to calculate from the resonant frequencies of these nonrotating combinations, values for the dangerous critical engine speeds when these propellers are rotated as in actual service. In our opinion these researches, although valuable, give less certain results than the direct determination of critical engine speeds with a given combination of engine and propeller in actual flight.

As a first step in making such measurements possible, we have designed and constructed an instrument, which, when mounted on the propeller vibrating apparatus at the Bureau, gives unmistakable indications of resonant vibrations when such vibrations are visually seen to be present. The theory of the instrument indicates that it will also function on a rotating propeller where visual observation is impractical. It is the purpose of this paper to describe this propeller-vibration indicator.

II. PRELIMINARY EXPERIMENTS

In a study of the performance of the propeller vibration apparatus, the motion of the shaft about its axis of rotation was measured by means of a mirror mounted on the shaft which reflected the light from a lamp onto a scale. It was observed that when the exciting frequency was such that resonant vibrations occurred, the amplitude of motion of the reflected spot of light was increased to many times that observed at higher or lower frequencies. This observation suggested the possibility of detecting dangerous propeller vibration by an instrument mounted on the engine shaft at the propeller hub which would respond to the torsional oscillation of the shaft about its axis.

Theoretically a wide variety of devices could be used. Optical and mechanical lever systems were considered impractical because of the difficulty of reading at long distances. Electrical distance-indicating devices would obviate that difficulty. Here also a wide variety of effects could be used, such as variations of electrical capacity, variation of magnetic reluctance, variation of electrical resistance, or the

[2] Air Corps Technical Report 3891. Study of Types of Vibration Possible in Aircraft Propellers. Lt. H. H. Couch. Sept. 21, 1933.

[3] If this picture of propeller failures is correct, safety cannot be guaranteed by a reasonable increase in cross section of the propeller blade, since such redesign merely shifts the resonant frequency to a new value. Moreover, while the presence of nicks in the surface of the blade may contribute to the failure, the failure would probably occur in any case if the engine speed were closely adjusted to one of the critical values.

electromagnetic generation of current. The instrument which seemed most promising was some form of electromagnetic generator.

Experiments were begun with a small d-c electric motor used as a generator. Two general arrangements were contemplated. In one, the field was to be stationary with respect to the airplane, and the armature rotated continuously. The torsional oscillation would cause a variation in speed, giving an alternating component in the current which could be separated by a transformer. In the other arrangement, both field and armature were to rotate with the propeller, a slight freedom of motion between the two being permitted, the free member being given a definite position, relative to the fixed member, by means of weak springs when at rest or in uniform rotation. Because of the inertia of the free member, a torsional vibration would generate directly an alternating current. The sensitivity was found to be ample, but the use of field magnets excited by electric current

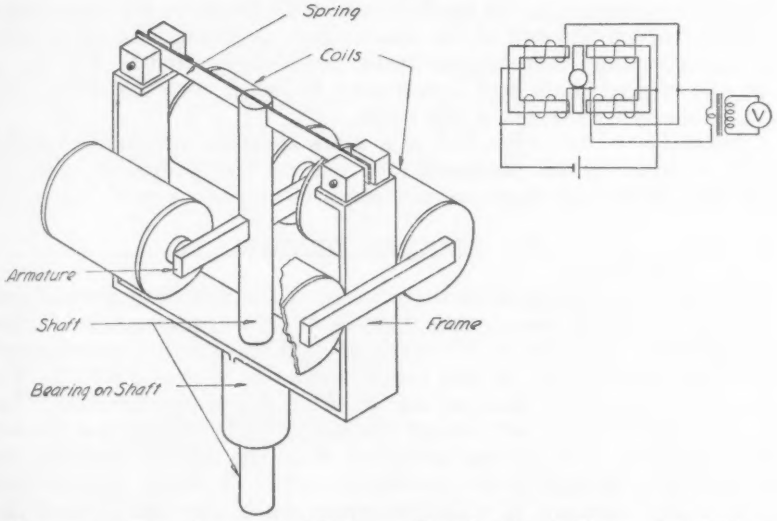


FIGURE 1.—*Experimental model of propeller-vibration indicator, first design.*

complicated the design. The mechanical mounting of the device on an actual airplane was likewise difficult, if not impractical.

A brief study was made of the possibility of using a field supplied by a permanent magnet, as in the ordinary magneto. No existing device was sufficiently small and sensitive to be readily adapted, and the design and construction of an entirely new generator appeared to be a long and expensive undertaking. Moreover, at this stage, a different type of generator appeared to be more promising.

III. FIRST DESIGN

In the experiments with a generator utilizing an electromagnetic field, accidental opening of the field circuit induced in the armature circuit a large current which burned out a sensitive thermal milliammeter connected in the armature circuit. This mishap suggested a bridge arrangement which was improvised from the four coils of two ordinary 20-ohm relays. The general arrangement is shown in figure 1. The motion of the armature generates in the four coils electro-

motive forces which are caused to send currents in the same direction through the indicating instrument by the bridge connection. The bridge connection likewise approximately eliminates the magnetizing currents from the meter circuit, although it is desirable to use a transformer as shown.

The armature must be maintained in the central position by means of springs sufficiently strong to overcome the magnetic pull. The stiffness of the springs together with the inertia of the moving system determines the natural frequency of oscillation of the instrument which should be as low as possible. Hence the armature is made the fixed member and the coils, cores, and pole-pieces are used to give the moving part a large moment of inertia. Since the motions to be measured are very small, it is advantageous to use fixed stops to prevent unnecessarily large travel so that weaker springs may be used than would be required if the armature came very close to the pole-pieces.

This arrangement can be made exceedingly sensitive for a given size. Its mounting on the end of the shaft offers no mechanical difficulties, but four electrical connections must be brought to it. For one of these the engine shaft and frame may be used, but the other three must be made by insulated slip rings.

A generator of this type but of a more compact mechanical design has been constructed, primarily for use on the propeller vibration apparatus where slip rings are not required.

IV. SECOND DESIGN

The first crude model of an instrument of the first design was shown to our associates in the electrical division for suggestions for further development. Dr. Frank Wenner outlined the general arrangement which was used for our second design shown in figures 2 and 3. The principle is essentially that of the Baldwin telephone receiver. The field is supplied by a permanent magnet, which magnetizes the soft iron pole-pieces. When the armature is in the central position, the magnetic flux through it is practically zero. A slight displacement causes a flux through it which reverses when the direction of displacement reverses. The coils in which the voltage is induced surround the armature on each side of the shaft and are connected in series. A stabilizing spring system is used as in the first design.

The instrument actually constructed was built around a magnet taken from an old electrical instrument. The air-gap between armature and pole-piece was 0.010 inch, and the motion was limited by stops to 0.004 inch in either direction. Each of the coils consisted of approximately 2,500 turns of no. 40 enameled wire, the direct current resistance of the two coils in series being 1,000 ohms. The indicating instrument used is a Weston model 600 rectifier type, with a range of 100 microamperes and impedance of the order of 3,500 ohms. Full-scale reading of the indicator corresponds to an angular velocity of the armature relative to the magnet of the order of ½ radian per second. A shunt is used to decrease the sensitivity when required. With these high resistances in the generator and meter, the slip-ring arrangement may be very crude and a long metallic ground return may be used without difficulty.

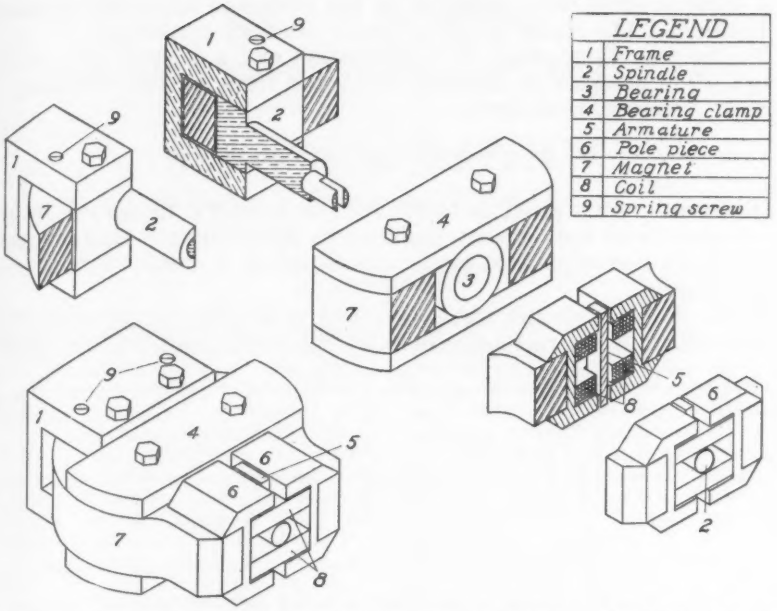
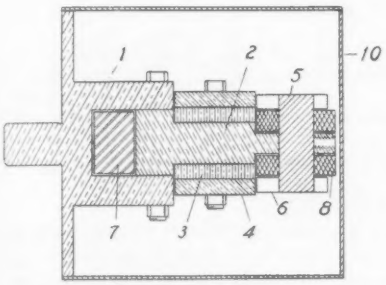


FIGURE 2.—*Propeller-vibration indicator, second design. Dissected view, cover removed.*



LEGEND	
1	Frame
2	Spindle
3	Bearing
4	Bearing clamp
5	Armature
6	Pole piece
7	Magnet
8	Coil
9	Spring screw
10	Cover

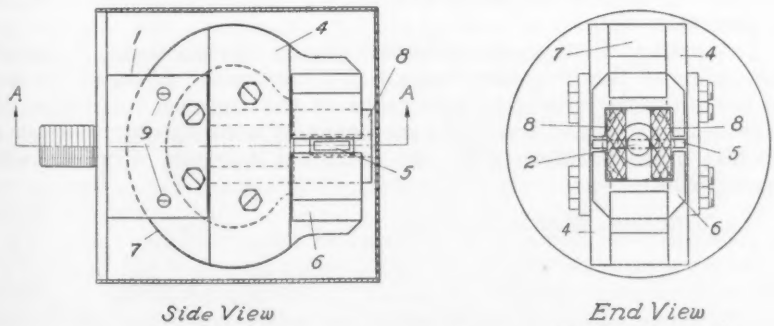


FIGURE 3.—*Propeller-vibration indicator, second design. Side view, end view, and section.*

A typical curve for a propeller on the vibrating apparatus is shown in figure 4. The sharp resonant peaks are very prominent.

By the use of one stage of amplification and a cathode-ray oscillograph, it is possible to observe the wave form of the variation of angular velocity, if desired.

V. FURTHER DEVELOPMENT

It appears easily possible to reduce the weight considerably below the 4 pounds of the present instrument by casting a magnet from some of the newer magnet steels which permit a greater intensity of magnetization.

While the instrument was developed primarily for the detection of vibrations of aircraft propellers, it has application in other fields

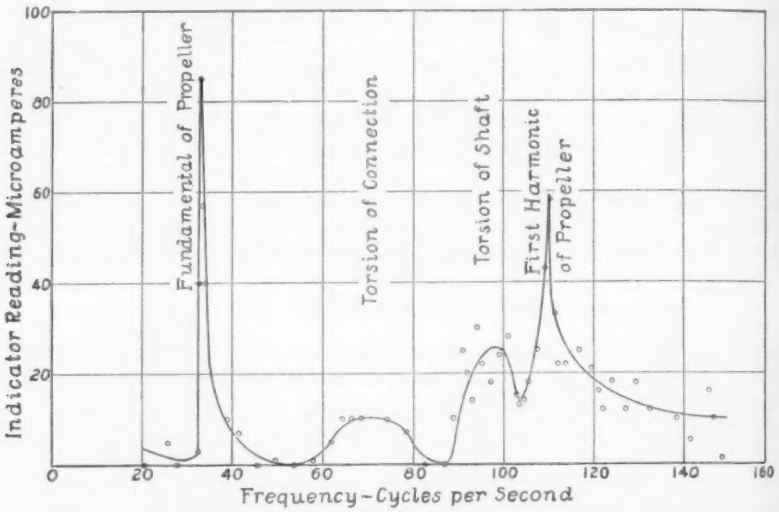


FIGURE 4.—*Typical curve for a propeller on the vibrating apparatus.*

where torsional vibrations are of interest. For example, we have mounted the indicator on an electric generator and on an electric motor. In each case, the indicator gives a reading increasing with load, and the frequency of the most intense vibrations corresponds to that harmonic of the speed of rotation which is equal to the number of armature slots.

The present instrument indicates clearly the presence of resonant vibrations of the propeller blade and torsional vibration of the shaft on the propeller vibrating apparatus at the Bureau. Arrangements have been concluded to try the indicator on a rotating propeller on an aircraft in cooperation with the National Advisory Committee for Aeronautics.

WASHINGTON, March 24, 1934.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP679

Part of Bureau of Standards Journal of Research, vol. 12, May 1934

HOSIERY TESTING MACHINE

By Herbert F. Schiefer and William D. Appel

ABSTRACT

The machine described in this paper provides a convenient means for measuring the behavior of a woman's full-fashioned stocking when the upper part of the leg of the stocking is repeatedly distended in a way which subjects it to forces similar to those which occur at the knee and at the garter clasps of a stocking in use. Two smooth "jaws" are inserted in the upper part of the stocking. It is held by two garter clasps attached at the welt and by a weight fastened to the ankle. The jaws are repeatedly separated and brought toward each other by a reciprocating mechanism in such a way that the circumference of the stocking, that is, the distance around the jaws, is varied between 13.3 and 21.3 inches. Means are provided for recording on a chart the relationship between the load exerted on the stocking and the circumference of the stocking for each cycle of loading and unloading. The number of cycles is recorded by a counter. The test may be continued until holes or runs are produced in the stocking.

Typical results of tests are given. The effect of laundering on the behavior of the stockings is also shown.

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I. INTRODUCTION

When, early in 1933, the General Federation of Women's Clubs undertook the development of a specification for women's full-fashioned hosiery as a basis for the labeling of standard grades, the federation requested the Bureau of Standards to provide suitable test methods. Among the properties for which tests were requested were elasticity, bursting strength, and ability to resist runs. Since existing test methods and equipment did not appear to be adequate for the purpose, a new testing machine was developed. This machine is described here and some typical results obtained with it are given. The results indicate that the machine should be of value not only for the purposes of the specification, but also for the study and control of hosiery in the course of manufacture. With suitable modifications, the machine should be useful for testing other types of knitted fabrics and garments.

A woman's stocking must be capable of considerable distention in the region of the welt and upper leg if it is to give satisfactory service. Further, it should be sufficiently elastic to accommodate itself to the shape of the leg of the wearer and it should not lose this elasticity and

become baggy after a period of use. A stocking is no longer satisfactory when a hole or run appears in it or when it ceases to fit the wearer. Failure occurs frequently at the knee of the stocking and at or near the point of attachment of the garter where maximum stresses are developed in the fabric.

These considerations led to the selection of the upper part of the leg of the stocking, including the welt, as the portion to be tested. The possibility of testing specimens of the fabric cut from the stocking was considered, but there would arise the problem of how to clasp the specimen. Further, it was desired to test the whole article, including the seam, by subjecting it to forces similar to those acting on the stocking in use. This appears to have been accomplished in the test to be described. The magnitudes of these forces vary with the build of the wearer, the position assumed by her, the number and location of attachment of garter clasps, as well as the dimensions of the stocking and the nature of the fabric of which it is made. The forces in the machine test probably approach those likely to develop under the most drastic reasonable conditions of use.

The machine permits the upper part of the leg of a stocking to be repeatedly distended. It provides means for recording on a chart the relationship between the load and circumference for each cycle of loading and unloading. Stockings having constructions considered to be standard in the industry have not developed defects in 2,000 to 5,000 cycles on the machine. Inferior stockings develop holes or runs in a very few cycles.

II. THE MACHINE

The hosiery testing machine is shown in figure 1. The upper part of the stocking, *A*, is slipped over two jaws, *B* and *C*. Two garter clasps, *D*, which are attached to opposite sides of the welt, are connected through a spring to the toggle, *E*. The toggle is connected to the two jaws. A cord, to which is attached a weight, *W*, is fastened to the ankle of the stocking.

The surface of each jaw is polished. The cross section is semicircular. The diameter is 2 inches for a length of 8 inches and then gradually tapers off over the remaining 4 inches to the tip. The lower jaw, *B*, is fastened to a vertical rod, *G*, which in turn is connected through a connecting rod, *R*, to the crank disk, *H*, of the electric motor and reduction gear, *I*. The lower jaw is moved up and down by the motor at the rate of 60 cycles per minute. The amplitude of the movement of the lower jaw may be varied by varying the throw of the crank. The distance between the two jaws can be adjusted by the screw, *F*. For the standard test the minimum distance between the jaws is 3.5 inches and the throw of the crank is 2 inches. The minimum and maximum circumferences, distances around the jaws, are therefore 13.3 and 21.3 inches, respectively.

The upper jaw, *C*, is fastened to a vertical rod which in turn is supported by a disk, *J*, on the spring, *K*. The load which a stocking exerts on the upper jaw is transmitted by the rod to the top of the spring or it may be transmitted by the rod directly to the support, *M*, by rotating the disk, *L*, through a small angle. The compression of the spring is recorded on the chart, *P*, of stylograph paper by a steel needle fastened to one end of the lever, *N*. The contact between the

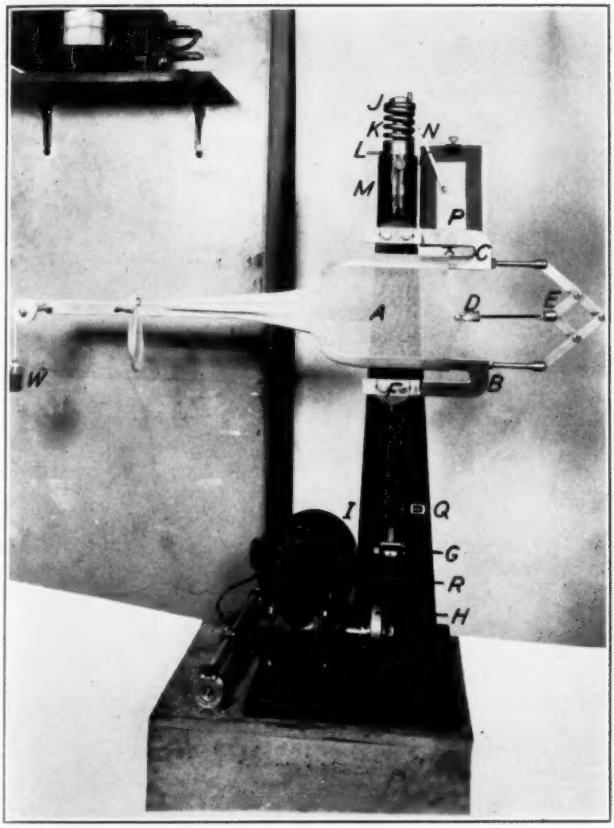

FIGURE 1.—*Hosiery testing machine with stocking in place partly distended.*

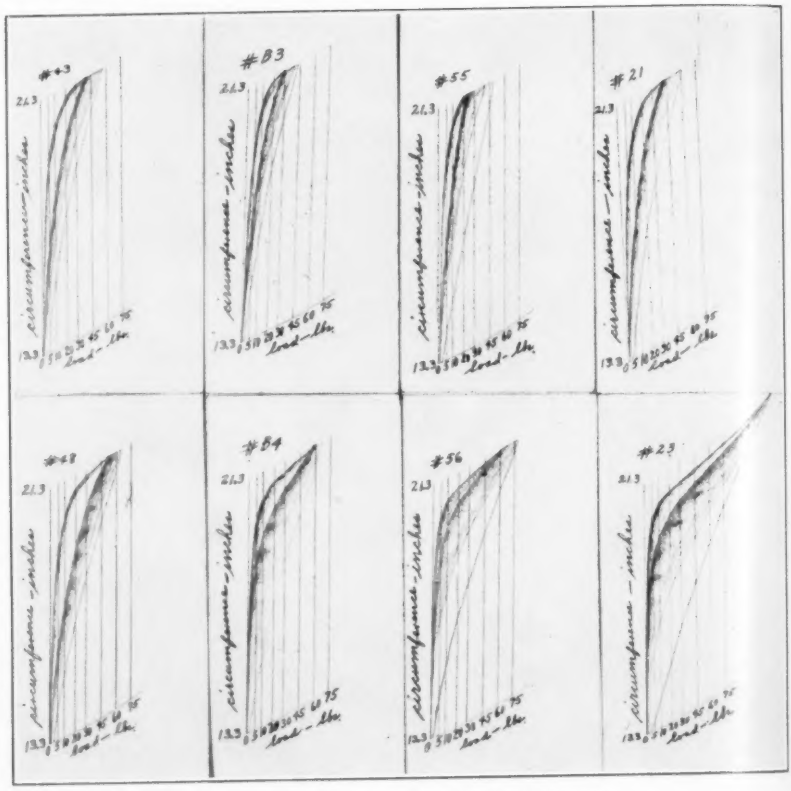

FIGURE 3.—*Typical records of silk hosiery.*

The top row is for stockings as received from the retail stores. The bottom row is for duplicate stockings after laundering. (See table 1.)

needle and the chart may be broken by a cam. The compression of the spring is magnified 15 times and is recorded as a circular arc. The chart, which is attached by an extension rod to G, is moved up and down simultaneously with the lower jaw. The movement of the lower jaw is recorded on the chart by a vertical line. The relationship between the load on the stocking and the circumference of the stocking is recorded as a closed curve for each cycle. The number of cycles is recorded by the counter, Q.

The tension which is exerted by each garter clasp varies with the weight, W, and with the maximum circumference. It is approximately equal to 5 pounds when the weight is equal to 1 pound and the maximum circumference is equal to 21.3 inches.

III. CALIBRATION

To calibrate the spring, K, loads are placed on top of the disk, J, and the corresponding compressions of the spring are recorded on the chart. The calibration shown in figure 2 is based upon 20 calibrations. The variation between calibrations is less than 1 percent. The vertical lines correspond to various loads, and the circular arcs correspond to various circumferences. A correction has been applied for the slight decrease in circumference due to the compression of the spring. For reading the load or circumference from the chart it is convenient to use a transparent photographic reproduction of the calibration.

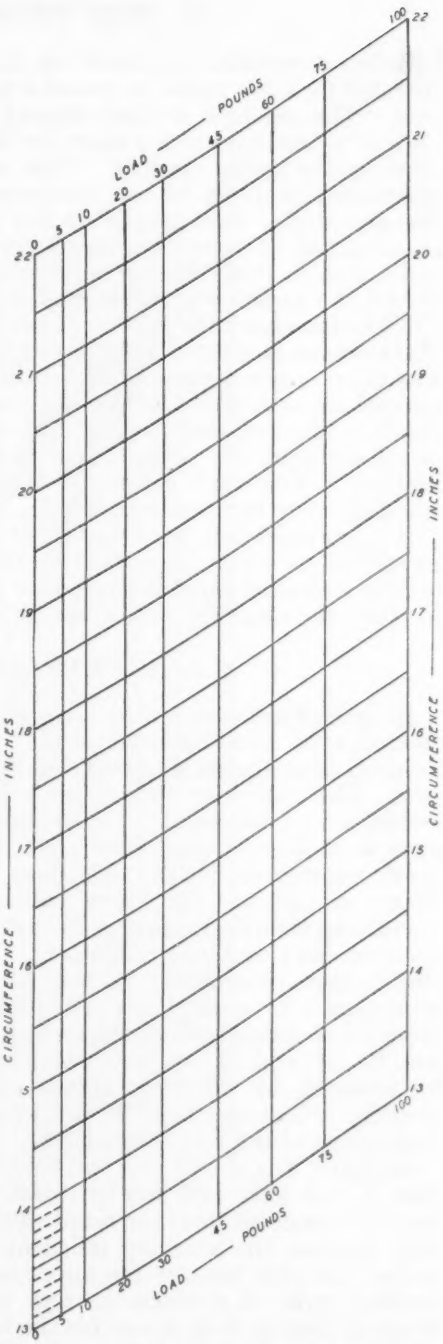

FIGURE 2.—*Calibration chart of the hosiery-testing machine.*

IV. TEST PROCEDURE

Before a stocking is placed on the jaws for test the machine is operated for a few cycles to record a vertical line corresponding to zero load. The machine is then stopped with the distance between the jaws at a minimum and a short arc is recorded on the chart by compressing the spring slightly. This arc denotes the position on the chart corresponding to the minimum circumference of 13.3 inches. The stocking is then placed on the jaws and the two garter clasps are attached to opposite sides of the welt midway between the jaws and 1 inch in from the top edge or selvage. The cord to which the weight of 1 pound is fastened is attached to the ankle of the stocking 2 to 3 inches above the bottom of the heel. The counter is set at zero. The machine is started and the stocking is repeatedly distended to a maximum circumference of 21.3 inches. Two hundred or any other convenient number of cycles are recorded on the chart, when the needle is lifted off and the load is transferred from the spring directly to the support, *M*. This change can be made without stopping the machine. The test is continued until a hole or run is produced in the stocking, or to any predetermined number of cycles, e.g., 1,000.

It is assumed that tests made with the hosiery-testing machine will be carried out on stockings that are in equilibrium with an atmosphere having a relative humidity of 65 ± 2 percent and a temperature of 70 to 80 F, the standard conditions for textile testing.

V. ILLUSTRATIVE TESTS

In figure 3 are shown the charts which were obtained by testing silk stockings of four different kinds. The stockings were tested as received from the retail stores, top row, and after laundering, bottom row. The stockings were repeatedly distended from 13.3 to 21.3 inches in circumference. The weight, *W*, was equal to 1 pound. The tests were discontinued after 1,000 cycles unless failure occurred at fewer number of cycles. The first 200 cycles are recorded on the charts, except no. 56, where failure occurred at 115 cycles. The laundering treatment appears to have a great effect on the relationship between load and circumference. This is particularly true of the chiffon type represented by nos. 55 and 56 and of the service type represented by nos. 21 and 23. After laundering a greater load is required to distend the stockings to a given circumference. Stockings nos. B4, 56, and 23 became permanently deformed or baggy as shown, for example, by the great increase in circumference at a load of 10 pounds. Stockings nos. 56 and 23 developed holes and runs at an early stage of the test (see table 1).

In figure 4 is shown the test record of a "skimped" silk stocking, that is, one knit with too little silk in one course or circumference, tested as received from the retail store. This record is of interest, not only because the stocking failed at an early stage of the test, 117 cycles, but also because the maximum load decreases with each succeeding cycle to a minimum and then increases again and finally becomes greater than it was for the first cycle. Because of the use of too little yarn in this stocking, the silk is stretched beyond the elastic limit during each cycle, the stocking becomes very baggy, and has a harsh, stiff feel in contrast to the soft, pliable feel of the untested

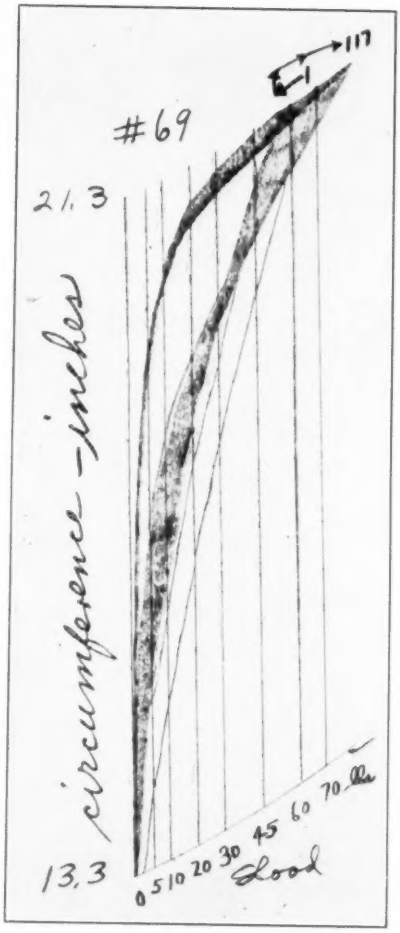

FIGURE 4.—*Test record of a skimped silk stocking.*

UNIV. OF MICH.

stocking. The variation of the maximum load with the number of cycles, namely, a gradual decrease for several cycles and then a gradual increase to a value greater than that of the first cycle, is probably partly due to a change in the character of the surface of the silk as indicated by the harsh feel and partly due to a change in the internal structure of the silk as indicated by the stiff feel. An X-ray study of the silk before and after testing should yield interesting and valuable information relative to changes in the internal structure of the silk.

VI. DISCUSSION AND APPLICATION

For a stocking to give satisfactory service it should meet the following requirements:

1. It should contain sufficient yarn in one course or circumference, that is, it should not be skimped.
2. It should have sufficient extensibility and elasticity, that is, it should stretch and yet not become permanently deformed or baggy as a result of stretching.
3. It should have sufficient durability, that is, it should not develop holes or runs when it is repeatedly distended.

A stocking which is skimped exerts a greater load when it is distended to a given extent than one which is not skimped but made from the same size yarn. Compliance with the first requirement can be determined, for a given weight stocking, by (a) specifying a maximum permissible load at the maximum distention of the first cycle, (b) specifying a minimum permissible circumference at a given load, e.g., 30 pounds, of the first cycle, and (c) specifying a maximum permissible amount of work expended during loading of the first cycle as given by the area under the loading curve and the zero load line.

When a stocking becomes permanently deformed or baggy during a test, the loading curves of the different cycles gradually approach the zero load line. Compliance with the second requirement for a given weight stocking can be determined by (a) specifying a maximum permissible circumference at a given load, e.g., 10 pounds, of the loading curve after a given number of cycles, e.g., 200 cycles, (b) specifying a minimum permissible value for the ratio of the work expended during loading of the 201st cycle to that expended during loading of the 1st cycle.

Compliance with the third requirement can be determined by specifying a minimum number of cycles, e.g., 1,000, which the stocking must withstand without the development of holes or runs.

In table 1 are summarized the results of the tests on four different kinds of silk stockings. The numbers correspond to the numbers contained on the test records shown in figure 3. The data show the great variations in the physical properties and quality of popular commercial stockings. They indicate the need of a comprehensive study of the effect of the various factors on the behavior of the stocking. A few of the factors which obviously will have an effect are the following: 1, size or weight of the yarn; 2, twist in the yarn; 3, nature of the fiber in the yarn; 4, total number of wales or loops in one course or circumference of the stocking; 5, gage or size of each wale or loop; and 6, nature and amount of finishing material in the stocking. The results of a systematic study of the effect of the various factors should be of inestimable value to manufacturers, distributors, and users of hosiery.

TABLE 1.—*Summary of typical tests of silk hosiery*

No.	Type	Retail price per pair	Condition of stocking at test	Maximum load 1st cycle	Circumference of stocking at a load of—		Work expended during loading		Ratio of Y/X	Number of cycles of test	Remarks
					30 lb. 1st cycle	10 lb. 201st cycle	1st cycle X	201st cycle Y			
		Dollars		*Pounds*	*Inches*	*Inches*	*In.-Lb.*	*In.-Lb.*	*Percent*		
43	Semiservice, A	0.69	As received	57	18.6	18.0	95	45	47	1,000	Not baggy and no failures.
48	Do	.69	Laundered	65	17.9	17.3	115	61	53	1,000	Do.
B3	Semiservice, B	1.00	As received	43	19.7	18.8	70	34	49	1,000	Slight bagginess and no failures.
B4	Do	1.00	Laundered	66	18.0	19.3	114	36	32	1,000	Baggy and no failures.
55	Chiffon, C	1.35	As received	48	18.3	18.7	97	33	34	1,000	Slight bagginess and no failures.
56	Do	1.35	Laundered	78	17.5	19.7	127	35	27	115	Baggy and failures.
21	Service, D	.79	As received	60	18.3	17.7	103	51	50	1,000	Not baggy and no failures.
23	Do	.79	Laundered	125	16.1	19.2	214	67	31	445	Baggy and failures.

The results given indicate what may be expected from the use of the hosiery testing machine.[1] The machine should be of value to manufacturers for the control of hosiery in the course of manufacture and for a systematic study of the effect of such factors as yarn size, yarn twist, hosiery gage, total number of wales in one course, degumming, dyeing, finishing, and laundering on the properties of the stocking. It should be useful to testing laboratories for conducting routine and commercial testing of hosiery. Finally, this machine provides a basis for specifying standard grades of hosiery in terms of performance and, therefore, should be of particular interest to the users of hosiery.

WASHINGTON, March 3, 1934.

[1] Drawings showing the details of construction of the hosiery testing machine may be obtained from the textile section of the Bureau of Standards upon request.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP680

Part of Bureau of Standards Journal of Research, vol. 12, May 1934

SIGNIFICANT VAPOR PRESSURE CONSIDERATIONS OF THE VAN SLYKE MANOMETRIC METHOD OF GAS ANALYSIS

By Martin Shepherd

ABSTRACT

The significance of vapor pressures in relation to the ***c correction*** of the Van Slyke manometric method of gas analysis is discussed. It is shown that the ***c correction*** changes with temperature in such a way that the determination of one such correction for a particular apparatus (and procedure) is inadequate. The prescribed Van Slyke technique may introduce errors amounting to several tenths of 1 percent in cases where the accuracy claimed is several hundredths of 1 percent. Other vapor-pressure considerations are discussed and possible errors pointed out. Two suggestions are offered to correct the difficulty, one of which involves a modification of the apparatus.

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INTRODUCTION

The development of satisfactory apparatus and methods for the analysis of the gases dissolved in blood has offered an unusually interesting problem. Among the investigations in this difficult and important field those of Van Slyke and his colleagues are outstanding. The manometric apparatus and methods of Van Slyke are extensively used for the analysis of dissolved gases; and these methods have been extended to include not only the analysis of many solutions by gasometric methods but also the macro- and micro-analysis of gas mixtures. A complete report of this work is given in "Quantitative Clinical Chemistry", vol. 2 (Methods), by John P. Peters and Donald D. Van Slyke (the Williams & Wilkins Co., Baltimore, Md., 1932). In the present discussion all references to details of the Van Slyke technique will be cited from this text.

Like all other methods of gas analysis, the Van Slyke manometric method is subject to a number of errors, most of them of small magnitude. And unlike some methods, that of Van Slyke is supplied with a number of painstaking procedures designed to eliminate

the inaccuracies caused by such errors. The purpose of this paper is to amplify one of the corrections prescribed and to point out that this correction is dependent upon temperature in such a manner that significant errors may sometimes occur when the correction is used as prescribed.

II. OUTLINE OF THE VAN SLYKE MANOMETRIC METHOD

A very brief résumé of the manometric method is presented for those who are not familar with the Van Slyke technique.

1. *Analysis of Dissolved Gases.* (For a complete account of these methods, the reader should refer to the text cited, pp. 269–442.)—The blood or other solution to be examined is taken into an extraction chamber over mercury, together with a suitable reagent, and outgassed by shaking under reduced pressure (the vapor pressure of the particular mixture present plus the pressure of the released gas at a volume of approximately 50 cc). The extraction chamber is calibrated at three fixed points, and the pressure (p_1) exerted by the liberated gas is measured by an attached manometer at one of these three constant volumes, after adjusting the meniscus of the solution to the etched mark defining the desired volume. A measured amount of gas-free reagent is then introduced, and when this has absorbed the desired component of the extracted gas mixture, the meniscus of the solution is adjusted to the same reference mark as before and the diminished pressure (p_2) read on the manometer. The difference, p_1-p_2, minus a correction $\boldsymbol{c}$, gives the pressure exerted by the gas removed by the reagent and affords the basis for calculating the amount of this gas in the measured sample of blood or other solution which was investigated. The significance of the ***c correction*** will be discussed in a moment.

2. *Analysis of Gas Mixtures.* (For a complete account of these methods, refer to the text cited, pages 106–160.)—The fixed volume at which the analysis is to be made is selected with reference to the amount of gas sample at hand. A pressure (p_o) is determined when the mercury meniscus is adjusted to the desired reference mark, and the extraction chamber contains no gas, but with the walls moistened by a film of gas-free water. The gas sample is introduced and the pressure (p_1) which it exerts is measured with the mercury again adjusted to the same reference mark. The pressure exerted by the sample is then calculated as $p_s=p_1-p_o$. A measured amount of reagent is admitted to remove one component of the gas mixture. When reaction is complete, the pressure (p_2) exerted by the residual gas is measured with the mercury meniscus again adjusted to the reference mark. The pressure exerted by the absorbed component is calculated as $p_s-K[p_2-(p_o+\boldsymbol{c})]$, where K is a factor to correct for the change in the fixed volume resulting from the addition of a known amount of reagent, and $\boldsymbol{c}$ is a correction similar to the one mentioned in the preceding paragraph.

III. SIGNIFICANCE OF THE VAN SLYKE *C CORRECTION*

Van Slyke explains the ***c correction*** for the two types of analyses as follows. Referring to the analysis of blood or dissolved gases, he states (p. 279):

"From the p_1-p_2 value observed it is usually necessary, for precise results, to deduct a correction which in the calculation formulae used is indicated by *c*.

The ***c correction*** is obtained by performing a blank analysis, in a manner directed for each type of determination. The p_1-p_2 value found in the blank constitutes the ***c correction.*** The ***c correction*** may be the sum of two components. One of them is a slight amount of gas which may be yielded by the reagents themselves. The other component is the fall in the manometer reading caused, even when no gas is removed, by the introduction of a given volume of absorbent solution. The introduction of solution between the two manometer readings p_1 and p_2 lowers the p_2 value merely by increasing the volume of liquid between the mercury surface and the water meniscus [1] at the moment of reading. Thereby the level of the mercury surface in the chamber, and, hence, also in the manometer, is lowered. The extent of this effect can be determined by means of blank analyses, in which, with the same amount of reagents but no gas in the chamber, the usual amount of absorbent solution is admitted. The manometer is read, with the water meniscus[2] in the chamber at the same mark before and after the admission of the absorbent solution. The difference between the two readings measures this component of the ***c correction.***"

It is also pointed out that the shape of the chamber will influence the value of this correction, which must accordingly be determined for each apparatus.

The ***c correction*** applied to methods for the analysis of gas mixtures is of the same nature, but since the mercury meniscus rather than that of the solution is always adjusted to the reference mark, the correction is of opposite sign. Concerning this type of analysis, Van Slyke states (p. 116):

"After the CO_2 has been absorbed"— (Author's note: this is, of course, the first component of respired air to be removed)— " the pressure exerted by the residual O_2+N_2 at 49 cc volume would be inexactly calculated as p_2-p_o. The zero manometer reading without any gas present is, on account of the 1 cc of NaOH solution present, slightly higher than the p_o observed at the beginning of the analysis with neither gas nor solution in the chamber. The weight of the short column of water in the chamber presses on the mercury there and in consequence raises the height of the mercury column in the manometer tube required to hold the meniscus in the chamber at the 50 cc mark. The ***c correction*** required for this effect varies somewhat with the shape of the bottom of the chamber and the consequent height of the column of 1 cc of solution. The correction is determined as follows: The p_o is determined, with the chamber free of both gas and visible amounts of water, as described on page 107. Then 1 cc of 1 *N* sodium hydroxide is admitted as described for absorption of CO_2, the chamber is evacuated till the mercury falls to the 50 cc mark, and the air is extracted from the solution by shaking the latter 1 minute. The extracted bubble of gas is ejected from the top of the chamber without loss of solution, as described on page 279. The chamber is again evacuated and the mercury meniscus is brought to the 50 cc mark. The manometer is again read. The difference between the two readings is the ***c correction.*** To determine ***c*** within 0.1 mm, one makes several check readings of p_o, and also several of p_o+c with the 1 cc of solution in the chamber. Once determined, the ***c correction*** serves for all analyses in which the same chamber is used."

This quotation is particularly significant to the present discussion, since the technique as prescribed by Van Slyke was followed in obtaining the data to be presented.

Van Slyke states that the ***c correction*** (as defined for the two types of analysis in the above quotations) is made up of one or both of two components. These he defines as follows: (p. 116), (1) "The weight of the short column of water [3] in the chamber pressing on the mercury there", or (p. 280), (1a) "the fall of the mercury surface in the chamber when absorbent solution is added." Case (1) applies to gas analysis, when the mercury meniscus is adjusted to the reference mark and the solution is above the mercury; case (1a) applies to the analysis of

[1] The term "water meniscus" should really be designated "solution meniscus", since the liquid is actually a water solution of various substances, and its saturation pressure is not exactly that of pure water.
[2] See footnote 1.
[3] See footnote 1.

dissolved gases when the solution meniscus is adjusted to the reference mark. The second component is (p. 279), (2) "A slight amount of gas which may be yielded by the reagents themselves."

In addition to the two components mentioned by Van Slyke, there is a third component which contributes to the total difference in pressure represented by this ***c correction.*** This is the lowering of vapor pressure with the introduction of the absorbing solution. The present discussion is directly concerned with this vapor pressure lowering.

The true nature and effect of the ***c correction*** can be shown by following through the procedure for the determination of CO_2 in respired air. In the following, p (with appropriate subscripts) will be used to identify the manometer pressures noted in Van Slyke's test (actual pressures—not merely readings of one arm of the manometer), and P (with subscripts) to identify the actual gas pressures or saturated vapor pressures. The subscript H_2O designates saturated water vapor, and the subscripts CO_2, O_2, and N_2 designate pressures exerted by these gases. The subscript H_2O' designates the saturation pressure of water over the normal sodium hydroxide solution (after reaction with CO_2). The height and density of the normal sodium hydroxide are expressed as h and d, respectively. The volumes at which pressures are measured before and after the introduction of the hydroxide are designated as V_1 and V_2, respectively. (It is assumed that temperature is constant, and that equilibrium is always attained.)

A pressure p_0 is measured at V_1 when the extraction chamber contains saturated water vapor, but with no gas or water over the mercury. Hence,

$$p_0 = P_{H_2O}. \tag{1}$$

The respired air is admitted and a pressure p_1 measured at V_1. It follows that

$$p_1 = P_{H_2O} + P_{CO_2} + P_{O_2+N_2}. \tag{2}$$

The pressure exerted by the sample (P_s) at V_1 is correctly given by

$$p_1 - p_0 = P_s = P_{CO_2} + P_{O_2+N_2}. \tag{3}$$

The hydroxide solution is admitted and CO_2 is removed. The residual pressure p_2, measured at V_2, is

$$p_2 = P_{H_2O'} + \frac{hd}{13.6} + (P_{O_2+N_2})_{V_2}. \tag{4}$$

Since

$$(P_{O_2+N_2})_{V_2} = \frac{V_1}{V_2}(P_{O_2+N_2})_{V_1} \tag{5}$$

$$p_2 = P_{H_2O'} + \frac{hd}{13.6} + \frac{V_1}{V_2}(P_{O_2+N_2}). \tag{6}$$

Subtracting (6) from (2):

$$p_1 - p_2 = P_{H_2O} - P_{H_2O'} - \frac{hd}{13.6} + P_{CO_2} + P_{O_2+N_2} - \frac{V_1}{V_2}(P_{O_2+N_2}). \tag{7}$$

Solving for P_{CO_2} in (7):

$$P_{CO_2} = P_{H_2O'} - P_{H_2O} + \frac{hd}{13.6} - P_{O_2+N_2}\left(1 - \frac{V_1}{V_2}\right) + p_1 - p_2. \tag{8}$$

Solving for $P_{O_2+N_2}$ from (6):

$$P_{O_2+N_2} = \frac{V_2}{V_1}\left(p_2 - P_{H_2O'} - \frac{hd}{13.6}\right). \tag{9}$$

Substituting this value in (8):

$$P_{CO_2} = p_1 - P_{H_2O} - \frac{V_2}{V_1}\left(p_2 - P_{H_2O'} - \frac{hd}{13.6}\right). \tag{10}$$

The equation given by Van Slyke (for the computation of P_{CO_2}) is

$$P_{CO_2} = P_S - P_{O_2+N_2} \tag{11}$$

or

$$P_{CO_2} = p_1 - p_0 - \frac{V_2}{V_1}[p_2 - (p_0 + c)]. \tag{12}$$

Substituting P_{H_2O} for p_0 from (1):

$$P_{CO_2} = p_1 - P_{H_2O} - \frac{V_2}{V_1}(p_2 - P_{H_2O} - c). \tag{13}$$

If P_{CO_2} is correctly given by both (10) and (13), then

$$c = \frac{hd}{13.6} - (P_{H_2O} - P_{H_2O'}). \tag{14}$$

The first term on the right-hand side of (14) represents the hydrostatic head, and the second term represents the vapor pressure lowering. Since, in the present work, the influence of any dissolved gas upon c was eliminated by using gas-free water and solutions, a term for the effect of such dissolved gas was not included in the equation.

In an analogous derivation of c for the case of blood gas analysis, which is not complicated by the factor expressing change in volume (since the meniscus of the solution is always adjusted to one fixed reference mark), one obtains the expression

$$c = \frac{hd}{13.6} + (P_{H_2O} - P_{H_2O'}). \tag{15}$$

where P_{H_2O} and $P_{H_2O'}$ really represent the vapor pressures of the liquid (e. g., blood) from which gas was extracted, and of the mixture of this liquid with the absorbing reagent, respectively. If the reagents were not gas free, a term should be added to equation (15) which would take this into account.

It is of course a fundamental requirement of such gasometric methods that all quantities of gas which are directly compared during an analysis be reduced to the same condition of temperature, pressure (or volume), and humidity. Van Slyke undoubtedly had this in mind, and made no mention of a vapor pressure lowering (in connection with the determination of ***c corrections***) evidently because he considered this to be negligible. He does mention the possibility of error from such a source in connection with the use of a 5 N sodium hydroxide solution for the determination of carbon dioxide in whole blood, under circumstance which do not permit dilution of the reagent with the 0.1 N lactic acid solution already present (p. 285 of his text). The same sort of error is cleverly dodged in his technique for air analysis (p. 115), which prescribes the determination of oxygen, after absorption with a 4 N solution of potassium hydroxide containing sodium thiosulphate, by measurement of the residual nitrogen rather than by direct measurement of the oxygen. Thus the residual nitrogen is represented by the difference in pressure readings after the absorption of the oxygen, and after ejection of the residual nitrogen but retaining the reagent used to absorb oxygen. The oxygen is then obtained by difference. The reason for this step was not given, probably since it was thought to be obvious enough. However, this very point has been overlooked in at least one case which recently came to our attention, wherein the analyst was erroneously determining oxygen directly.

The determination of carbon dioxide, however, does not depend upon such a procedure to eliminate this error. Instead, reliance is

evidently placed upon the fact that the vapor pressure of a solution of 1*N* sodium hydroxide will not greatly differ from that of water. This is reasonably true, except for the fact that the lowering of vapor pressure (with addition of normal sodium hydroxide solution) increases with temperature so that the saturation-pressure curves for water and the hydroxide solution diverge appreciably at temperatures much above 20 C. It consequently follows that the determination of the actual value of ***c*** is dependent upon temperature, and the ***c correction*** determined at one temperature is not necessarily satisfactory for other temperatures. Thus the determination of the ***c correction*** of a particular apparatus once for all, as suggested, may not be adequate. The data to be presented will illustrate this point.

In addition to the above, the vapor pressure lowering as a function of temperature becomes larger in cases where the specified 4 *N* and 5 *N* reagents are used in the analyses of dissolved gases. Thus a ***c correction*** obtained when these reagents are used may be subject to error with change of temperature unless the reagents are successfully diluted with solutions already present in the extraction chamber. When any gas is in the extraction chamber, it may not be possible to dilute the stronger alkaline solutions satisfactorily, since they are admitted from the top of the chamber, where a small amount just under the inlet stopcock may exert an appreciable effect on the vapor pressure of the system.

IV. METHOD FOR DETERMINING THE EFFECT OF TEMPERATURE ON *C CORRECTIONS*

The effect of temperature on the value of this correction can be shown experimentally by repeating the technique prescribed by Van Slyke (already noted) over the range of temperature which may be expected in the ordinary laboratory. The temperature of this laboratory varies from about 20 to 31 C. This condition may appear extreme to those located in more desirable climatic surroundings, but it is not strange to anyone who has occupied a laboratory in Washington. This range of temperature was accordingly selected as significant.

The data were obtained for the following solutions, which are reagents used by Van Slyke.

1 *N* sodium hydroxide.

4 *N* potassium hydroxide containing 15 g of sodium thiosulphate per 50 cc (filtered and protected from air).

5 *N* sodium hydroxide.

In every case the solution was thoroughly shaken in the extraction chamber.[4] In addition, this procedure was repeated a number of times during the course of a series of observations in order to insure the maintenance of this condition, and check readings were taken thereafter. The pressures reported represent the average of at least three readings agreeing within 0.1 mm.

The mercury meniscus was adjusted to the reference mark in all cases. The height of the solution above the mercury was measured by means of a cathetometer, the density of the solution determined, and the hydrostatic pressure of the solution calculated therefrom in

[4] This procedure is supposed to remove all measurable amounts of dissolved gas.

order to establish the contribution of this factor to the total change in pressure or ***c correction.*** In addition, pressures were determined in the case of the 1 *N* sodium hydroxide both with solution present and expelled, so that the latter series of observations gave a direct reading of the vapor pressures of this solution without the added effect of the hydrostatic head of the solution.

Observations were made with the mercury meniscus adjusted to both the 50 cc and 2 cc marks. These two series represent the conditions existing during macro- and micro-analyses, respectively. The 0.5 cc mark was not used, since the mercury meniscus, rather than the meniscus of the solution, was adjusted to the reference mark and 1 cc of solution was over the mercury.

All measurements of pressure were made under conditions such that the temperature of the water in the jacket surrounding the extraction chamber and that of the room were equal (within 0.1° C) and so maintained over considerable periods (1 hour or more). It was found that no reliable results could be obtained unless such a temperature equilibrium was established, even though the temperatures of room and jacket were brought to the same value by the method suggested by Van Slyke. Data to illustrate this point and the possible errors involved will be given.

The pressures reported are in mm of mercury (and are not merely readings of one arm of the manometer). The zero of the manometer scale was obtained for both of the reference marks used, by means of the cathetometer.

The data obtained are presented in the form of curves where observed pressures are plotted against corresponding temperatures. These are in effect vapor-pressure curves, with an added component in some cases which results from the effect of the hydrostatic head of the solution. The curves are designated as follows:

Those marked *V* 50 refer to pressure readings taken with the mercury meniscus adjusted to the 50 cc mark, and those marked *V* 2 are corresponding pressures taken with the mercury adjusted to the 2 cc mark.

Curves marked P_{H_2O} represent pressures observed with no gas present in the chamber and with a film of gas-free water moistening the walls, but with no visible water. These curves are accordingly the vapor pressure curves of pure water, and are shown to be in agreement with known data.

Curves designated as P_{1N} represent pressures taken with no gas in the extraction chamber and with the walls moistened by a 1 *N* solution of sodium hydroxide, with no visible amount of solution. The curves marked P_{1N+S} represent pressures observed under the same conditions, but with a measured volume (1 cc) of solution over the mercury. The latter curves include the effect of hydrostatic pressure.

Curves designated as P_{4N+S} represent pressures noted with no gas in the extraction chamber, but with 1 cc of the 4 *N* potassium hydroxide solution containing sodium thiosulphate (according to previously noted formula) present. Those marked P_{5N+S} indicate pressures observed under the same conditions with a 5 *N* solution of sodium hydroxide.

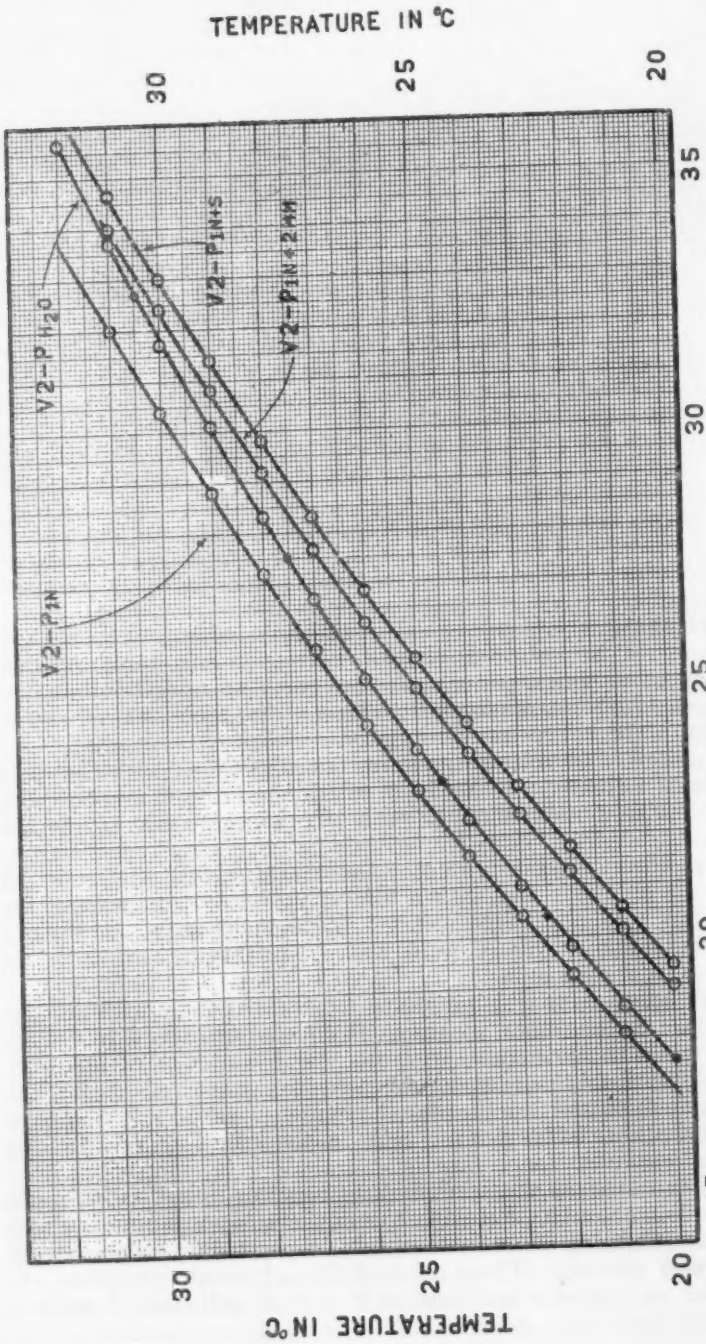

FIGURE 1.—*Vapor pressure data for water and pressures observed with the 1 N sodium hydroxide solution at the 2 cc volume.*

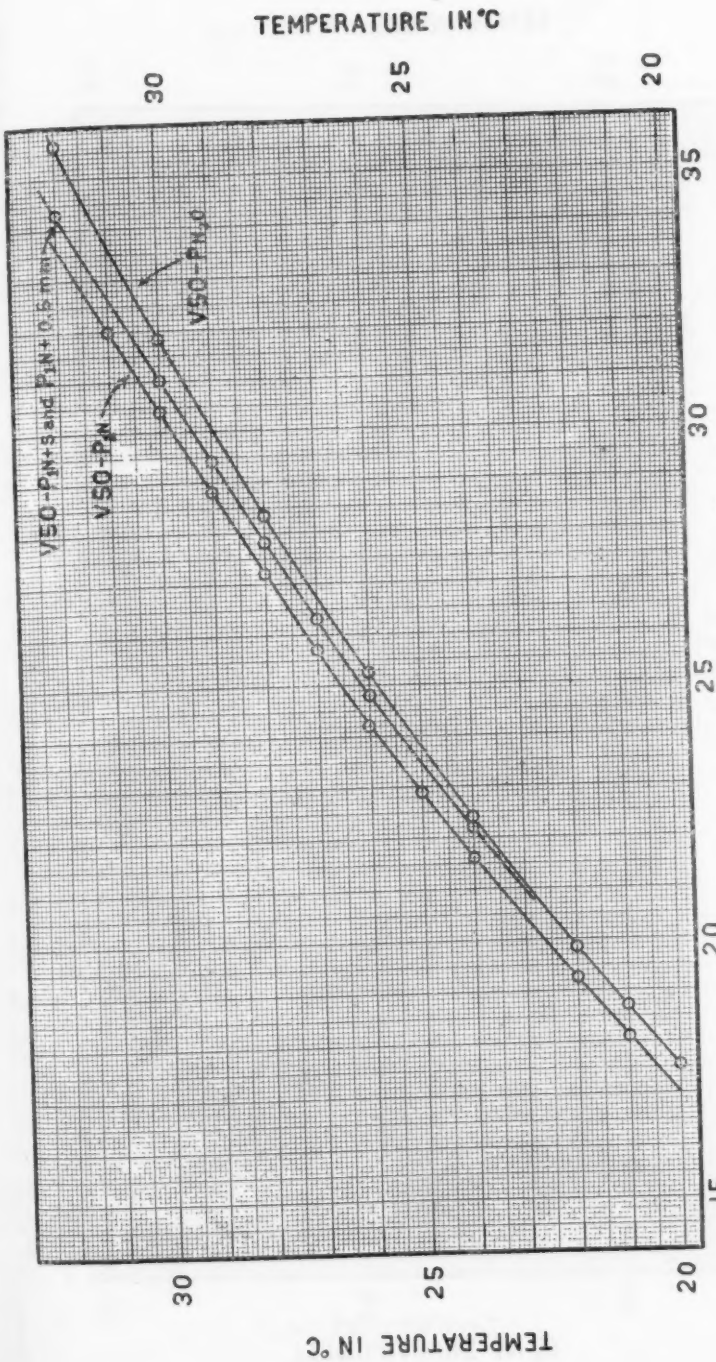

FIGURE 2.—*Vapor pressure data for water and pressures observed with the 1 N sodium hydroxide solution at the 50 cc volume.*

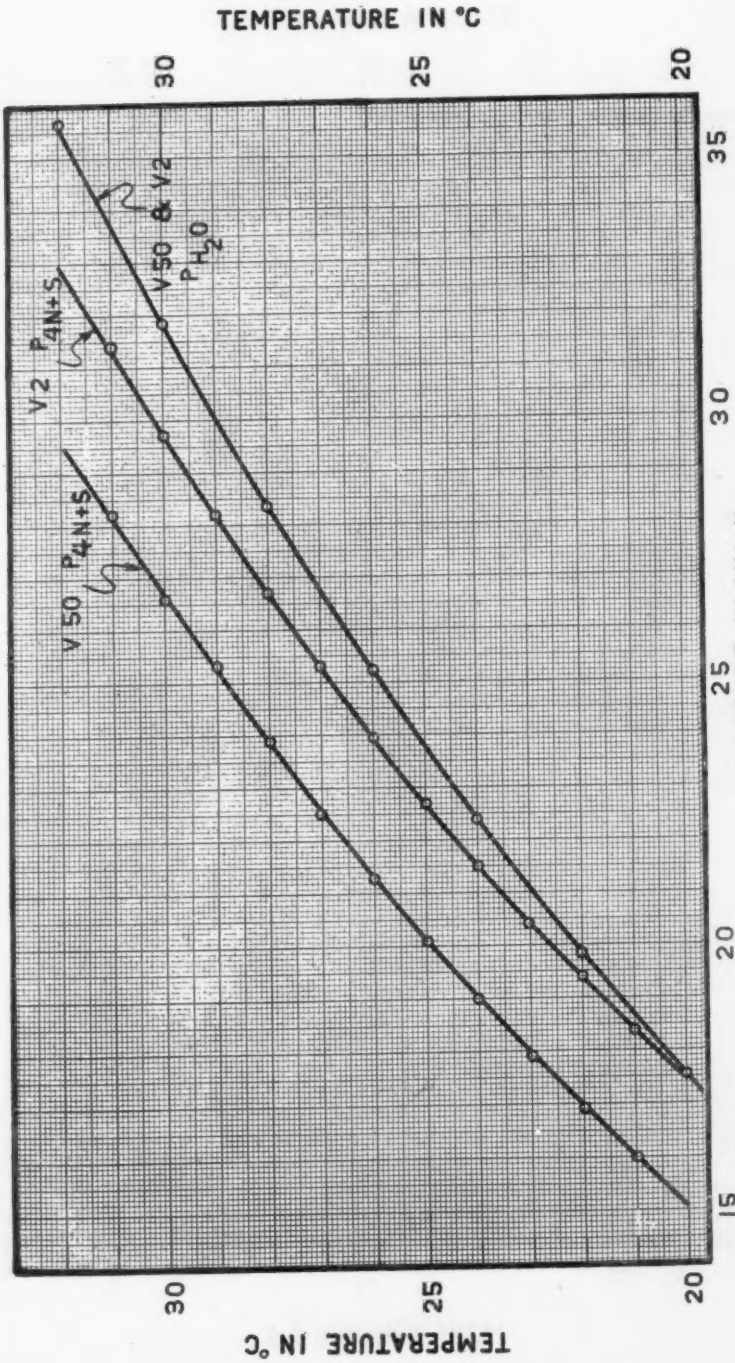

FIGURE 3.—*Vapor pressure data for water and pressures observed with the 4 N pot assium hydroxide+sodium thiosulphate solution at 2 cc and 50 cc volumes.*

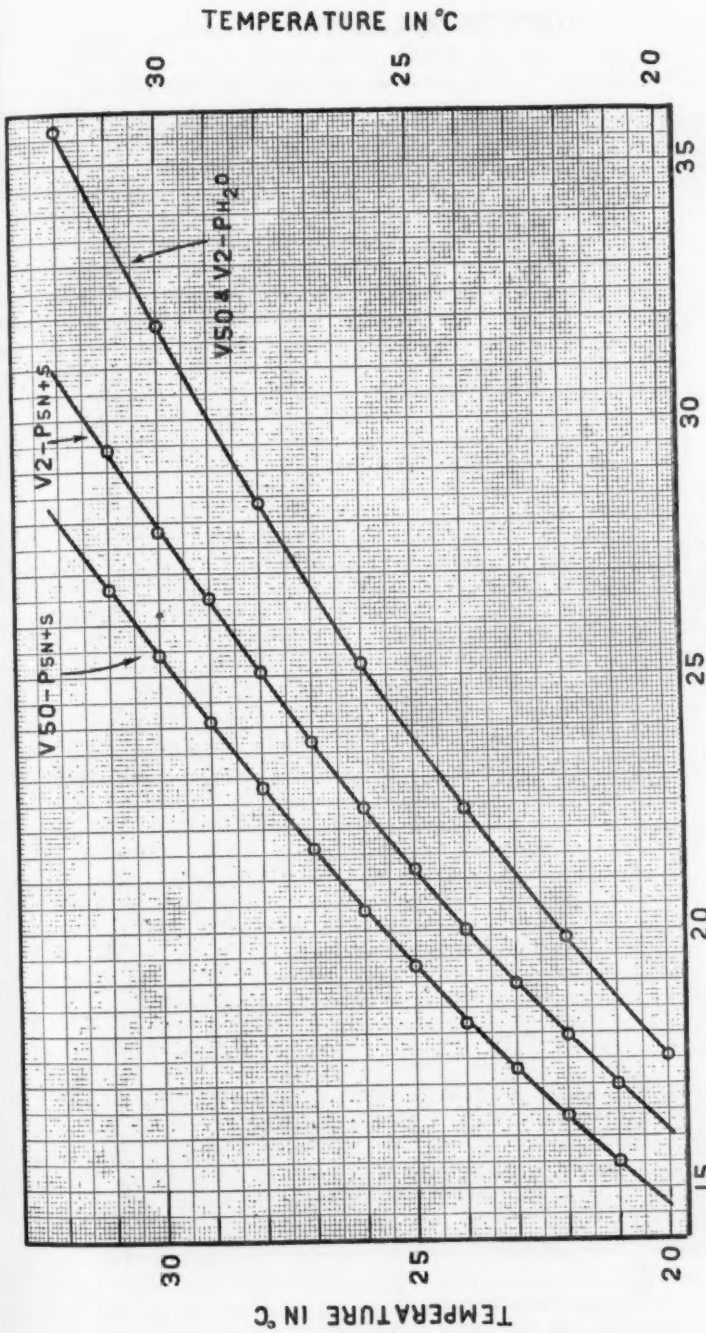

FIGURE 4.—*Vapor pressure data for water and pressures observed with the 5 N sodium hydroxide solution at 2 cc and 50 cc volumes.*

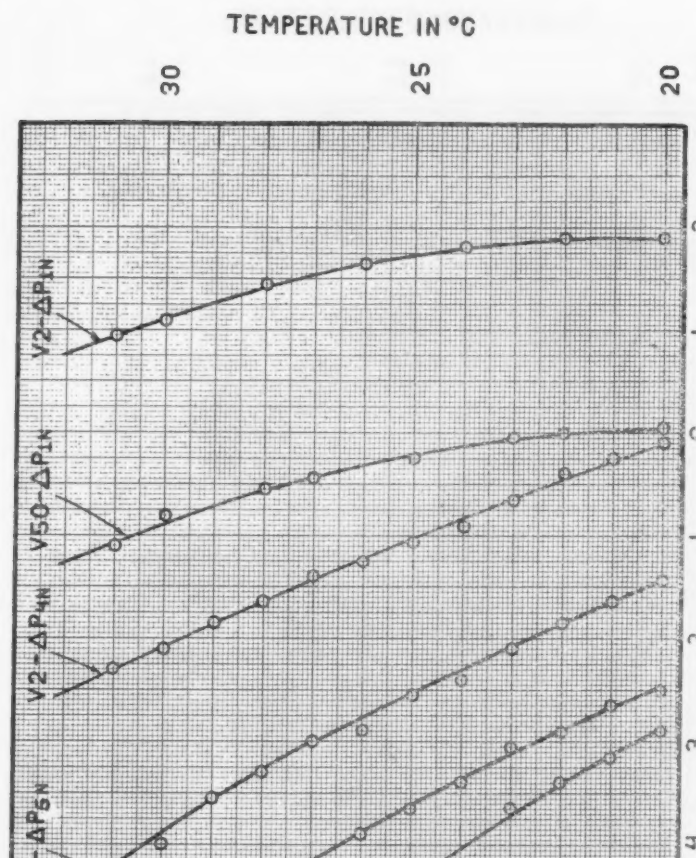

FIGURE 5.—*Values of the* **c** *correction at various temperatures.*

Curves for 1 *N* solution represent actual **c** *corrections* as applied to the analysis of gases (e.g., respired air).
Curves for the 4 *N* and 5 *N* solutions do not represent actual **c** *corrections* for the analysis of dissolved gases, but indicate the maximum errors which might occur if these solutions are not successfully diluted by the prescribed techniques.

V. DATA OBTAINED WITH THE 1 *N* SODIUM HYDROXIDE SOLUTION

This reagent is used to remove carbon dioxide, both in the analysis of gas mixtures, and from gases extracted from blood and other liquids. In the former case, the gas sample is measured when saturated with water vapor, while the residual gas remaining after absorption of carbon dioxide is measured at the saturation pressure of the reagent. The lowering of vapor pressure which occurs with the introduction of the reagent is small, but significant. The ***c correction,*** taken for the purpose of correcting for the hydrostatic head of reagent, will also correct for this lowering of vapor pressure at the particular temperature existing within the system at the time the ***c correction*** was measured. It will not correct for this lowering of vapor pressure for any other temperature at which the apparatus may be used in subsequent analyses. Whether or not the resulting error attains significance will depend upon the degree of divergence of the curve representing the vapor pressure of pure water from that representing the vapor pressure of the reagent, or from the vapor pressure of the reagent plus its hydrostatic pressure. The latter divergence represents the Van Slyke ***c correction.***

Data obtained for normal sodium hydroxide are given in figures 1 and 2, where the temperatures existing are plotted against the corresponding pressures. The curves of figure 1 represent the data for the volume 2 cc, and those of figure 2 for the volume 50 cc.

Referring to figure 1, the curve marked $V2-P_{H_2O}$ is the vapor pressure curve for pure water, and represents the p_o pressures of Van Slyke. The open circles represent values obtained experimentally with the apparatus employed, and the closed circles correspond to values given in International Critical Tables. The experimental values agree with the accepted data. The curve marked $V2-P_{1N}$ represents the experimental values obtained for the vapor pressures of the 1 *N* sodium hydroxide reagent. The divergence of these two curves is immediately noted.

The two sets of data just mentioned should not depend upon the fixed volume selected for the measurement, since no gas or visible amount of reagent is present. With 1 cc of reagent above the mercury, the values obtained will differ for the 2 cc and 50 cc fixed volumes, since the hydrostatic pressures are not equal at the two reference points. The curve marked $V2-P_{1N+s}$ represents values for the blank analyses when the 2 cc volume is chosen. It will be noted that at 20 C the value of P_{1N+s} is 19.4 mm, and the vapor pressure of water (P_{H_2O}, or p_o of Van Slyke) is 17.5+mm, a difference of 1.9 mm; but at 31 C, the value of P_{1N+s} is 34.7, and the vapor pressure of water is 33.7 mm, a difference of 1.0 mm. Thus if the ***c correction*** was obtained for the apparatus once for all at one of these temperatures, and analyses were subsequently conducted at the other temperature, the ***c correction*** would be in error by about 1 mm. The percentage error involved would depend upon the initial pressure exerted by the sample. This is usually about 500 mm, making the error about 0.2 percent. The accuracy claimed for the method is 0.05 percent (see page 113 of text), or, in case of the isolation method of Van Slyke, Sendroy and Liu (see p. 119), it is thought an accuracy of 0.0001 percent is attained. Under these circumstances, 0.2 percent becomes

significant. The case selected is, of course, extreme. If the analyst were fortunate enough to have obtained a ***c correction*** at say 25 C and performed an analysis at 26 C, the error would be about one tenth of the former one under like conditions. It should, however, be remembered that a lower initial pressure exerted by the sample will increase the error.

Referring again to figure 1, the curve $V2-P_{1N+2mm}$ is of interest. This represents the values for the vapor pressures of the 1 N solution (curve $V2-P_{1N}$) corrected for the hydrostatic pressure of the solution. The latter value was obtained by measuring the height and density of the solution and converting to mm of mercury. It will be seen that these values are slightly lower than those obtained by measuring the pressures with the solution over the mercury, although the two curves are nearly parallel. The difference is of the right order of magnitude to be explained by differences of capillarity. Corrections for capillarity are large in a tube of 4 mm diameter (which is the case at the 2 cc interval). It is worthy of note that the ***c correction*** obtained for 30 C was 1.1 mm, whereas the measured hydrostatic head of the solution was 2 mm.

Figure 2 illustrates corresponding data for the 1 N solution when the 50 cc fixed volume was chosen. In this case the hydrostatic pressure of the solution as measured was only 0.6 mm, and the values for the vapor pressures of the 1 N solution corrected for this figure lie along the curve of the observed values for the pressure P_{1N+s}. The differences between the P_{H_2O} and P_{1N+s} values are negligible at the lower temperatures, but the two curves diverge to give a ***c correction*** of 1 mm at 31 C, so that the error involved in assuming ***c*** independent of temperature is of the same order of magnitude as the one discussed for the $V2$ values.

VI. DATA OBTAINED WITH THE 4 *N* POTASSIUM HYDROXIDE SOLUTION CONTAINING SODIUM THIOSULPHATE, AND THE 5 *N* SODIUM HYDROXIDE SOLUTION

These data are illustrated graphically in figures 3 and 4 and are given for both the 2 and 50 cc fixed volumes. It is at once noted that any solution approaching such concentrations in the extraction chamber would cause large errors if ***c*** is assumed to be independent of temperature. For example, in the case of the 5 N solution at the 50 cc volume, ***c*** is about -2.9 mm at 20 C and about -6.9 mm at 31 C. The difference of 4 mm over an initial pressure of 400 mm represents an error of 1 percent, which is certainly too great to fit into this scheme of analysis. Such errors are probably never encountered in actual practice if the prescribed techniques are closely followed. The actual magnitude of the errors which do occur will depend upon the extent to which the reagent is successfully diluted with other solutions which may already be in the extraction chamber, and the complete removal of all traces of the reagent from under the upper stopcock of the extraction chamber. It must also be remembered that ***c***, while always the same general type of correction, is itself different for the many procedures described by Van Slyke. The determination of each constituent, in each type of analysis of dissolved gases, may have a different ***c***.

VII. CHANGE OF *C CORRECTIONS* WITH TEMPERATURE

Figure 5 represents graphically the differences observed between the P_{H_2O} values and those for the three reagents when 1 cc of the solution was above the mercury. These are the ***c corrections*** for the 2 cc and 50 cc volumes, and are plotted against temperature. If the ***c correction*** is obtained at one temperature and applied thereafter at any other temperature, the percentage error is determined by reading the value of ***c*** at the second temperature, subtracting from the first value obtained, and dividing this difference by the initial pressure exerted by the gas sample.

It should be remembered that the ***c corrections*** as derived do not include the component designated by Van Slyke as the small amount of gas which may be yielded by the reagents themselves. This is true since all the reagents employed were gas-free. Considering this component of the ***c correction,*** the value of the whole correction as usually applied may become doubtful if blanks are not performed with each analysis, since the reagents may be expected to hold varying amounts of gas in solution under different conditions of temperature and pressure, and these amounts, though small, exert decided effects on the pressures in small volumes.

VIII. EFFECT OF A DIFFERENCE OF TEMPERATURE BETWEEN THE WATER JACKET AND THE ROOM, AND THE ERROR WHICH MAY RESULT

The upper stopcock of the Van Slyke apparatus and a very small portion of the extraction chamber connected thereto extend above the water jacket. Liquid located on the walls of this portion of the apparatus exerts a decided effect on the resultant vapor pressure of the entire system. The tendency is, of course, for the resultant saturation pressure to be very nearly that of the solution at its coldest point. The following experiment illustrates this. The walls of the extraction chamber were moistened with gas–free water, with no visible amount of water. The room and the water in the jacket were held at 20.2 C. The observed pressure at 2 or 50 cc was 17.8 mm, which checks the value for the saturation pressure of water at that temperature. The jacket was then surrounded with a warm towel until the thermometer within the jacket registered 22.6 C. The room temperature, recorded at the same level (about 1 foot distant) was now observed to be 20.5 C. The pressure under these conditions was 18.4 mm, which is closer to the vapor pressure of water at 20.5 C (18.1 mm) than at 22.6 C (20.6 mm). The jacket was allowed to cool to the laboratory temperature. Readings taken were: Room, 20.2 C; jacket, 22.0 C; p, 17.9 mm; (P_{H_2O} = 17.8 mm at 20.2 C). Room, 20.2 C; jacket, 21.0 C; p, 17.8 mm; (P_{H_2O} = 17.8 mm at 20.2 C). Room, 20.1 C; jacket, 20.6 C; p, 17.8 mm; (P_{H_2O} = 17.7 mm at 20.1 C). In every case the significant temperature, based upon the observed vapor pressure, was that of the room rather than the jacket. When the room was heated, observations were made as follows: Room 23.5 C; jacket 23.1 C; p, 21.2 mm; (P_{H_2O} = 21.2 mm at 23.1 C).

It is consequently very important that the jacket temperature and laboratory temperature be closely equal, rather than no further apart

than 1° C, as specified (see p. 278 of text). Furthermore, the glass parts of the apparatus protruding from the jacket should be in temperature equilibrium with the room. Otherwise, an error will be made in correcting the pressure exerted by the gas sample for any change in the vapor pressure of water. Thus in the above case, when the jacket temperature was read as 21.0 C and the vapor pressure corresponded to a temperature of 20.2 C, an error of 0.9 mm would have been made when the correction was applied for the vapor pressure of water, and this in a case where the temperatures of room and jacket differed by only 0.8° C. At higher temperatures the error increases, so that a difference of 1° C at 30 to 31 C might involve an error of 1.9 mm, or nearly one half of 1 percent if the pressure exerted by the original sample had been 400 mm.

IX. CONCLUSION

Two suggestions follow naturally after consideration of the data presented.

1. The Van Slyke ***c corrections*** may be determined over the entire range of laboratory temperatures, and the appropriate correction selected for the particular analysis on hand.

2. The Van Slyke apparatus may be modified by placing two parallel chambers in the water jacket, one to function as an extraction and reaction chamber, and the other as a fixed volume buret.

The latter procedure would possess several additional advantages. It would always be possible to avoid redissolving some portion of an extracted gas sample, for which the correction is troublesome and not always satisfactory. This could be achieved by transferring the liberated gas from the extraction chamber to the buret under the pressure at which the extraction occurred. Each reagent could be freed from gas in the apparatus before bringing the gas mixture into the reaction chamber. Physical solution of components of the gas mixture in the reagent could be reduced for macro-analyses and almost avoided for micro-analyses. The various fractions of the gas mixture would always be accurately measured under the same condition of humidity. The measurement of gas volumes (or pressures) would always be made by adjusting a clean mercury meniscus to a reference mark, thus avoiding obscure solution menisci. Solutions from which gas samples were extracted, as well as reagents subsequently employed, could be expelled from the extraction chamber at each step of the analysis. This technique would permit straightforward clean reactions with no interference, either chemical or physical, from accumulating mixtures of various liquids that have already served their purpose in the analysis. Reagents of any desired strength could be employed. There would be no hydrostatic pressures to correct for, and the ***c correction***, as well as all others applied by Van Slyke, would merely resolve into a simple correction for the change of pressure of the gas and saturated water vapor with any change of temperature which might occur during the analysis.

WASHINGTON, February 14, 1934.

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A SENSITIVE INSTRUMENT FOR MEASURING THE AIR PERMEABILITY OF PAPER AND OTHER SHEET MATERIALS

By F. T. Carson

ABSTRACT

The new instrument contains a permeability cell of novel design, in which an annular cell surrounds the inner testing cell. By means of this arrangement the usual error from edge leakage is eliminated through the bypassing of the leakage air around the measuring apparatus. The pressures are so adjusted that there is no lateral pressure gradient at the boundary of the test cell and hence no leakage into it. A special pressure regulator has also been designed to maintain a very steady pressure drop across the instrument. The air flow is measured by means of a capillary flow meter, containing four carefully calibrated capillary tubes. The accurate range of the instrument is more than ten thousandfold and approximate measurements can be made over a millionfold range of air permeability values. Since the time element is taken care of in the calibration, tests of relatively impermeable papers are almost as rapid as those of the more porous variety. Results are reproducible on an identical area to within a few tenths of 1 percent. The instrument is well adapted to the testing of leather and some other sheet materials. It will accommodate sheets not thicker than half an inch and it is not necessary to cut the material in order to test it.

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I. INTRODUCTION

Notwithstanding the manifold significance of the air permeability of paper and fiber board, the literature on the measurement of this property reveals a field imperfectly explored and replete with differ-

ences of opinion about the influence of such experimental conditions as the pressure difference across the sheet, the area and thickness of the specimen, the duration of the test, the temperature and relative humidity of the enveloping atmosphere. There are practically no established standards in this field.

Under the program for the investigation, development, and standardization of methods and apparatus for evaluating the properties of paper, an investigation of the air permeability of paper was begun at the instance of the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry, which is interested in establishing a standard method of measuring the air permeability of paper and fiber board.

In addition to furnishing information applicable to the formulation of standards in apparatus, procedure, and units of expression, it was anticipated that the investigation would throw some light on the nature of the fibrous structure in a sheet of paper.

The investigation logically divides itself into two parts: The selection or development of a suitable measuring instrument; and the study of the behavior of paper and fiber boards under different experimental conditions and with reference to the theory of the flow of air through minute passages. The provision of an adequate measuring instrument is dealt with in this paper, whereas the other phase of the investigation will form the subject matter of a second publication.

II. THE PROBLEM AND THE PRELIMINARY SURVEY

The requirements in the investigation of variables in the measurement of air permeability, and the bearing of the behavior of these variables upon the structure of paper and upon the problem of standardizing the testing method, demand an instrument having a small experimental error and a range sufficient for the testing of a considerable variety of papers and fiber boards. A survey was first made of designs of apparatus described in the literature to see if any of these instruments could be adapted to the rather exacting requirements of the proposed investigation. The literature reveals a score or more of air-permeability measuring devices adapted to the testing of paper and other fibrous sheet materials. Space permits only the most cursory description of these various designs. References appear at the end of this paper for the convenience of the reader who wishes further details.

According to Herzberg (14),[1] the earliest form of apparatus was that of Winkler-Karstens, made somewhat on the order of a diminutive gas-meter prover with the paper specimen replacing the upper end of the bell. In this group (group 1) are also the apparatus of Gurley (28), Lhomme et Argy (17), and Barr (1). About three fourths of the designs which have been described make use of some form of measuring flask by which the displacement of a liquid measures the volume of air passing through the specimen, and apparently have been patterned after different forms of gas-measuring and standardizing apparatus. The gas-measuring burette (group 2) is represented by the apparatus of Privett (21), that of Bekk (2), and another of uncertain origin (12, 22). The standardizing flask (group 3) is perhaps most frequently represented in the designs offered. In the

[1] The numbers in parentheses here and throughout the text refer to the references at the end of the paper p. 584.

apparatus of Sindall (26), Ivanov (15), Bergmann (4), and Silvio (25), the specimen is attached to the flask or disposed in such manner that the inflowing liquid displaces air from the flask through the specimen (subgroup 3a). In the apparatus of Schopper (14) and that of Potts (20), air which is drawn through the paper displaces liquid into a measuring flask (subgroup 3b). The apparatus of Dalen (14) and the Weaver-Pickering apparatus (7) make use of a wet meter to measure the volume of air drawn through the paper (group 4). Emanueli (11), who placed a capillary flow meter in series with the specimen, appears to be the first to make use of the inferential type of gas meter (group 5) in measuring the air permeability of fibrous sheets. The pressure drop through the capillary and that through the paper he measured with water manometers. He then evaluated the rate of flow of air through the paper from these data and a constant of the capillary. This double-flow-meter arrangement has since been used in several instruments: Larson, Nelson, and Bratz (16); Schiefer and Best (23); Doughty, Seborg, and Baird (8); Edwards (9); and Marsh (18). Instruments representative of most of these groups are available from instrument dealers and were studied during the early stages of this investigation.

Most of the apparatus in groups 1, 2, 3a, and some in group 5 are not designed to permit properly conditioned air to flow through the specimen. The study of the effect of experimental variables requires an adjustable pressure difference across the specimen, which can be held constant during a given test. Instruments of group 1 confine the pressure difference to a single, fixed value. The methods employed in groups 2, 3, 4, and 5 to produce a continuous flow of air through the specimen entail either continuous or erratic changes in the pressure difference, unless some means is provided to steady it. A variety of schemes have been used to maintain a constant pressure difference.

The more successful of these employ some form of air vent submerged in water so that a change in line pressure results in a change in the rate of venting rather than in a change in the pressure head. This method, however, is characterized by a continuous pulsation in the pressure difference as the air bubbles form and break away at the end of the submerged vent. Others make use of overflow tanks, large tanks for the displacing liquid, or large reservoirs in the air line, which lessen, but do not eliminate, fluctuations in pressure differences. The auxiliary apparatus is always bulky and not entirely successful. The instruments of groups 1, 2, 3, and 4 require the measurement of the time of the relative displacement of a given volume of liquid, which results in a lengthy and tedious test for papers which are not very permeable. Instruments of the first four groups are, for the most part, suited for the measurement of only a rather narrow range of air permeability. In most of the instruments the area tested is very small. It is difficult to estimate the possible precision of the various instruments, but the precision of those available for study seemed inadequate for the present purpose. Without exception, the accuracy of the score or more of instruments is questionable, chiefly because of leakage or uncertainty in the effective area of the specimen. With few exceptions, no method is provided or suggested for testing the apparatus against leakage.

In general the design of the permeability cell is ineffective in that it fails to insure that all of the air which goes through the nominal test

area, and only this air, passes also through the measuring apparatus. This deficiency becomes serious when one is testing materials having rough or uneven surfaces, materials that are not very permeable, or comparatively thick materials. When these characteristics are all found in a single material the existing designs of testing apparatus are taxed entirely beyond their ability to yield a reliable result. Leakage through the edges of the specimen or between the specimen and the clamping surfaces is sometimes very large. During this preliminary study of available instruments, instances occurred of leakage errors as great as the permeability value itself. It is ironical that, while a number of instruments depend upon clamping the sheet between smooth, annular surfaces to prevent leakage, a recent apparatus (2) is designed to determine the roughness of paper by measuring the rate of this very leakage between the surface of the paper and the clamping surface. In some instruments rubber gaskets and heavy clamping pressure are used to minimize leakage at the edges. These precautions may suffice for thin, smooth papers in which the leakage through the edges of the specimen is negligible, but even in this case the creeping of the rubber under pressure introduces some uncertainty into the effective area tested. The use of gaskets with thicker materials, however, cannot prevent appreciable amounts of air from passing through the edges of the specimen. The most elaborate precautions have been taken by Wilson and Lines (31), Edwards (9), Privett (21), Marsh (18), and Barr (1), who designed their permeability cells so that the edges of the specimen are entirely enclosed and sealed off from the atmosphere. This design lessens, but does not eliminate, movement of air in that portion of the specimen confined between the clamping surfaces. Air must still move outward in the upper levels and inward in the lower levels of this region (if the pressure drop is inward). Although perhaps small for thin sheets, the resulting increase in effective area must be appreciable for thicker materials. Experiments with fiber boards indicate that this tendency is especially pronounced in materials having a laminated structure. The design of Barr, in which the annular enclosed space is evacuated to approximately the pressure within the permeability cell, errs in the opposite direction and leads to permeability values which are too low, because the lateral pressure gradient from the upper periphery of the test area to the annular space must cause a portion of the air which should emerge into the permeability cell to be dissipated into the annular space. One can but repeat the complaint of Potts (20) that all the familiar air permeability testing devices fall short in some respect.

III. DEVELOPMENT OF SUITABLE INSTRUMENT

The preliminary survey revealed the inadequacy of available instruments for a thorough investigation of variables in the measurement of the air permeability of paper, and indicated the following major requirements in an improved design: Means of eliminating leakage at the edges of the specimen, and means of testing the apparatus as a whole against leakage; means of maintaining a truly constant pressure difference across the specimen while air, conditioned according to the standard method, is drawn through the specimen; a range of at least several thousandfold to cover the usual types of

papers and fiber boards; a precise means of measuring the flow of air through the specimen. A very desirable feature to facilitate the investigation is a design permitting fairly rapid testing of materials of low permeability. An additional desideratum is a fairly large specimen interposed in the air stream.

1. DESCRIPTION OF NEW INSTRUMENT

Figure 1 illustrates schematically the apparatus devised for the investigation, and figure 2 is a photograph of the instrument.

(a) PERMEABILITY CELL

The specimen S is clamped between two elements, each of which is composed of a central cavity or cell C and an annular cell DD separated by a circular wall terminating in a narrow edge E, less than half a millimeter wide at the line of contact with the specimen. A rubber ring G makes a seal between the annular cell DD and the atmosphere. Conditioned air at atmospheric pressure is accessible to the upper surface of the specimen above both the lower cells C and DD. By means of an air pump P, air is drawn simultaneously from C and DD, the relative flow being adjusted by valves W and Z (for coarse and fine adjustments) until the two menisci of manometer N are at the same level. Since the horizontal pressure difference across the boundary between the two cells is zero at any level, there can be no edge leakage into or out of cell C. Only the air which comes through that part of the specimen supported above the cell C is admitted to the measuring device, air reaching DD from the upper surface or through leakage at the edges being by-passed around the meter. The pressure drop through the specimen is measured with the manometer L.

LIST OF FIGURE NUMBERS AND LEGENDS

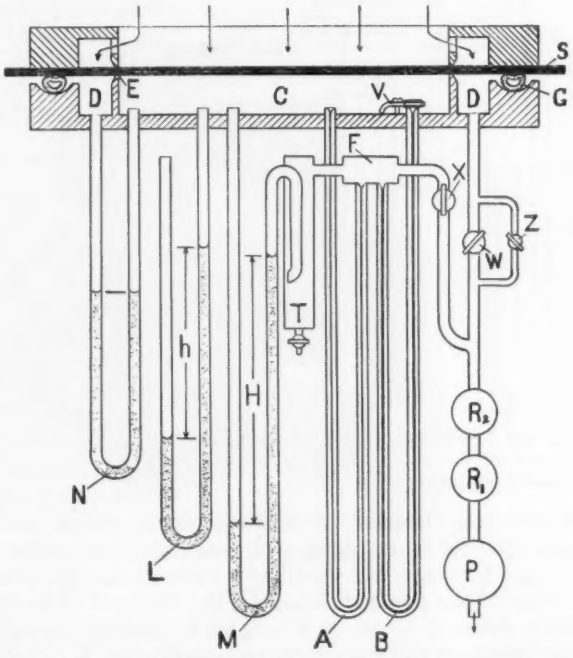

FIGURE 1.—*Schematic drawing of the air permeability instrument developed at the Bureau of Standards*

The area of the aperture of the cell C is 100 cm². That appreciable sagging or stretching of paper over this large area may be prevented, the specimen is supported by two concentric rings (not illustrated) with very thin contact edges.

Heavy clamping pressure is not necessary. It is sufficient that good contact is made between the specimen and the bounding edge E. In fact, tests made on a smooth, rather permeable paper without any pressure contact whatever on the specimen above the bounding edge E (the paper being held only by a narrow clamping ring directly above the rubber ring G) indicated that there was practically no movement of air across the clamping surface E when the menisci of manometer N were at the same level. Some detail of the clamping mechanism can be seen in figure 2. The clamping ring J is constrained to move vertically by guides in the ends of two L-shaped brackets K, and to register accurately with the permeability cell. It lifts high enough to accommodate any sheet material less than half an inch thick. Since it is always convenient, and sometimes necessary, to test a material without having to cut or specially shape it, the clamp is designed so that it is open on three sides when the ring is lifted. The clamping pressure, which is applied by the handwheel U at the rear, is transmitted through a Y-shaped rocker arm having contact at two opposite points on the clamping ring.

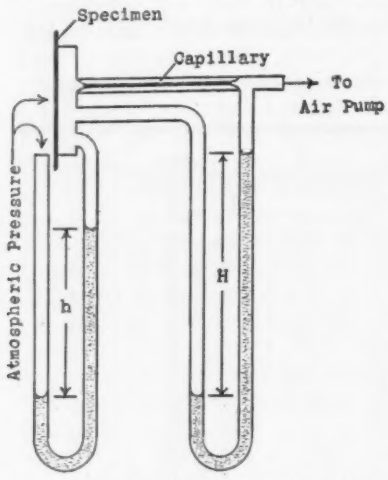

FIGURE 3.—*Double-flow-meter method used in measuring the air permeability of paper*

(b) MEANS OF MEASURING AIR FLOW

The inferential type of flow meter was chosen as preferable to any of the other types for measuring continuous flow of air through materials having such a wide range of air permeability values as paper and fiber boards. It is more versatile and lends itself to more rapid testing and to compactness in design. The double-flow-meter principle of measurement is illustrated in its simplest terms in figure 3, in which a capillary flow meter is placed in series with the specimen arranged as a diaphragm in another flow meter. If the rate of discharge through the capillary tube is known from calibration for all values of the pressure head H, the value of H in any given test immediately shows the rate at which air is passing through the specimen under the pressure difference corresponding to h. Actual measurements of volume and time are not necessary, since these are made once for all in the calibration. In figure 1 the calibrated flow meter consists of the manometer M and 4 capillary tubes of different capacities, of which only 2, A and B, are shown.

One end of each capillary tube and one limb of each manometer are connected directly into the bottom of the permeability cell. The other end of each capillary tube is connected into a hollow metal block F, leading to the air pump P. A trap T is placed between the manometer M and this hollow block to prevent the manometer liquid from inadvertently overflowing into the block and entering the capillary tubes. The manometer and trap are connected to the block at the end opposite to the exit to the air pump so that the moving column

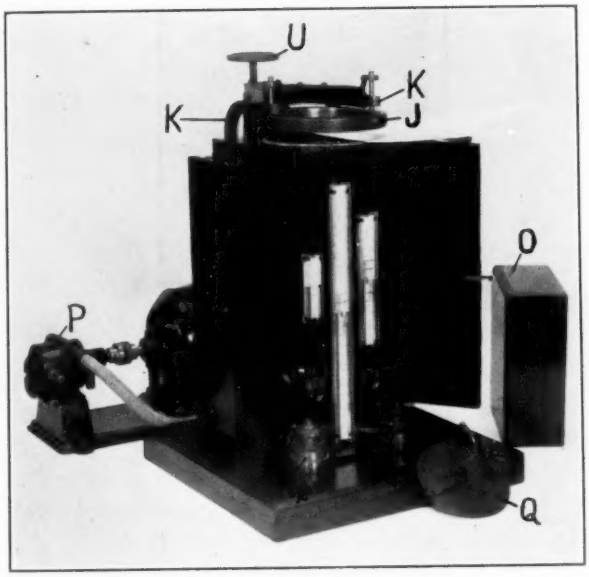

FIGURE 2.—*Photograph of the new instrument.*

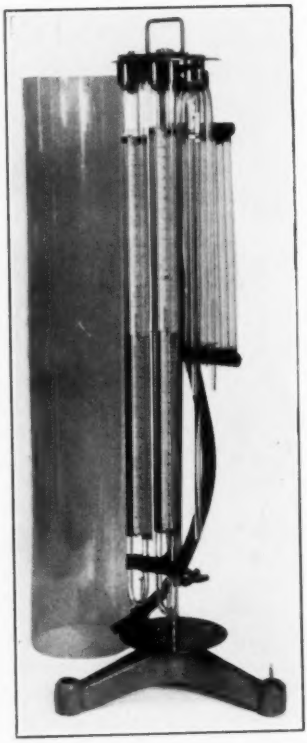

FIGURE 7.—*Calibrated flow meter for the rapid calibration of capillary tubes.*

of air in the hollow block is never a part of the connection between the manometer and the capillary in use.

One end of each capillary opening into the cell C is provided with a tab valve V, a detail of which is included in figure 4. A flat metal tab, over which is stretched a section of rubber tubing T, is pressed down on the end of the tubular projection P by means of a screw, making an airtight seal. Any one of the capillaries can be connected into the air stream simply by loosening the screw and turning the tab to one side. The tubular projections P serve also to prevent the manometer liquid from entering the capillary tubes from this end in case of accidental overflow into the permeability cell.

(c) GLASS-TO-METAL JOINTS

Although the connections of the glass capillaries and manometers to the metallic parts of the instrument can be made satisfactorily with good rubber tubing fastened to short metal tubes soldered into the metallic parts, a neater and more satisfactory glass-to-metal joint is illustrated in partial section in figure 4. The metal M to which the glass tube is to be fastened is drilled so as to leave a conical seat as shown. A short section of rubber tubing R is cut with a razor blade on a turning head so as to leave smooth ends. This rubber ring should fit snugly about the glass tube L and loosely in the hole in the metal. A collar C is forced by a yoke Y against the rubber ring, which in turn is squeezed into the annular conical space between the glass tube and the metal. A film of moisture applied to the rubber ring makes it seat more readily. The resulting joint is not only airtight, but is flexible and can be easily renewed when necessary. One yoke serves for two adjacent joints.

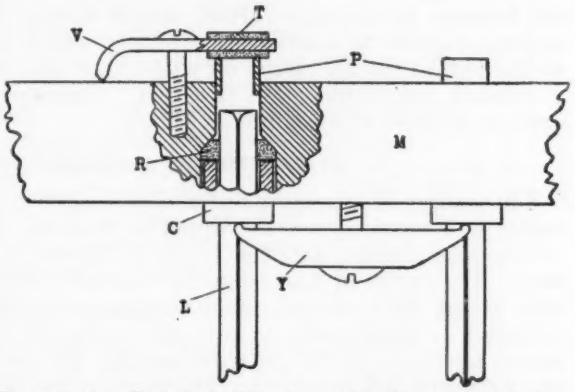

FIGURE 4.—*Detail of glass-to-metal joint used in connecting manometers and capillary tubes to the instrument.*

(d) MANOMETERS AND MANOMETER SCALES

In figure 2 the manometer on the left with the short scale corresponds to N of figure 1; the long manometer in the center, to M; and the one on the right, to L. Manometer N requires no scale other than a horizontal reference mark. The scales of manometers L and M are graduated in millimeters, and are backed by polished sheet metal, the vertical edges of which are bent so as to mirror the menisci of the manometer liquid just to one side of the manometer tubes in order that one may avoid parallax in reading the pressure heads. Since the scale readings are estimated to tenths of a millimeter, the graduations must be quite uniform. The scales are preferably engraved on metal with a dividing engine. Paper scales, however, may

be used if they are adjusted to the proper length by exposure in air of suitable humidity and then cemented to a metal backing with some such adhesive as cellulose acetate. The scales are fastened to the manometers with spring clips and are adjustable vertically for the zero reading. This adjustment, however, need not be exact, since the readings of the two limbs of each manometer are added to obtain the pressure head. Kerosene was chosen for the manometer liquid because water is likely to give false readings unless the manometer tubes are kept scrupulously clean.

(e) TESTING APPARATUS FOR LEAKAGE

The specimen S is replaced by a piece of sheet metal with a soft rubber gasket underneath. A partial vacuum is created in the apparatus and the stopcock X is closed. If there is a leak anywhere (except in the tab-valves) that would affect the air permeability results, it will be indicated by a drop in the head h of manometer L. As a test for leakage in the tab-valves, which should be made each time a change is made to a different capillary, cell C is left open at the top, all the capillaries are closed off with their tab-valves, a partial vacuum is created, and stopcock X is closed. Leakage will be indicated by a drop in head H of manometer M.

(f) SELECTION OF CAPILLARY TUBES

The range of pressure differences selected for the capillary flow meter is 5 to 25 g/cm^2, the upper limit being chosen chiefly for convenience in design, and the lower to insure precise manometer readings. The range of 5 to 10 g/cm^2 was selected for the pressure difference across the specimen, since this pressure difference should be kept as small as practicable to prevent undue stretching of the material tested and to simplify the expression of the results. The ratio of the two pressure differences can, therefore, vary through a tenfold range, and hence each capillary used in the instrument will suffice for a tenfold range of air permeability values if the air flow is approximately proportional to the pressure difference. It was found that most types of paper and fiber board lie within the air permeability range of 0.1 to 5,000 cm^3/sec/m^2/g/cm^2, and that this range could be fairly well covered with the new instrument by providing it with four capillaries having discharge rates of 0.01, 0.1, 1, and 10 liters per minute at a pressure difference of 25 g/cm^2.

It is preferable to have the bore of the capillaries as large as possible to minimize the chance of obstruction by foreign particles. A large test area contributes to the possibility of using larger bores for a given permeability range. The capillaries should be of glass that one may more readily detect obstructing particles, since the danger of fouling is the chief objection which has been offered to the use of capillary flow meters. The length should also be as great as practicable, since it must be very great in comparison with the diameter of the bore if the rate of discharge is to be even approximately proportional to the pressure difference. All but one of the capillaries in the instrument are about 2 feet long.

Capillary tubes of the required length and capacity were selected with the help of data published by Benton (3) so that the discharge

rates at a pressure difference of 25 g/cm² would be well below the critical velocity, since the calibration is very uncertain in the neighborhood of the critical velocity. It is not practicable to select the capillaries from dimensional measurements alone, since very small differences in bore make considerable differences in discharge rate. From a large number of capillaries a considerable number were selected having bores of approximately the desired size. The discharge rates of these were then roughly measured with a previously calibrated capillary flow meter. From these measurements it was possible to select three approximating the requirements enumerated above for the first three capacities. These were bent in a U-shape to conserve space in the instrument. For the largest capacity required a single capillary 2 feet long was not satisfactory, since the critical velocity was exceeded for the higher pressure differences. A satisfactory capillary was made by connecting in parallel a number of smaller capillary tubes, as illustrated in figure 5. Air enters through a short connection into a brass tube into which seven straight capillary tubes about a foot long are sealed with a cement specially recommended for sealing glass to metal. The air, after passing through the several capillary tubes in parallel, enters another section of the brass tubing and thence out through a longer connection. The design is such that the multiple-tube capillary can be connected to the apparatus in the same manner as the U-shaped capillary tubes.

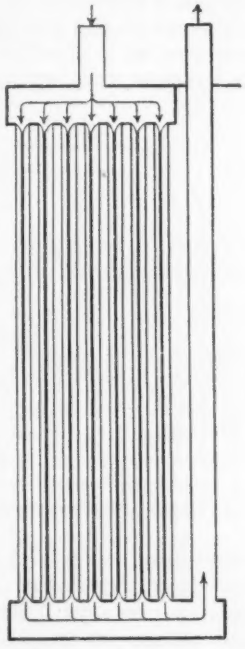

FIGURE 5.—*Multiple-tube capillary for the larger discharge rates.*

(g) PRESSURE REGULATOR

With manometer readings being taken to a tenth of a millimeter and the line pressure fluctuating over a range of several millimeters or perhaps a few centimeters, very exacting requirements are made of the pressure regulating device. The regulator shown in figure 6, a form of diaphragm valve, was designed especially for the requirements of the new instrument. A rubber diaphragm D closes one side of the chamber B, which is about 2 inches in diameter. A hollow post P is adjustable vertically with reference to the diaphragm by means of the nut N threaded over the upper end of the post. The joints are made tight by means of leather washers W, held under mechanical pressure. Air from the chamber B, can pass between the diaphragm and the end of the hollow post, through the orifice into the space H, and out through the hollow cylinder C to the air pump. The desired pressure difference across the air permeability instrument from A to B is obtained by moving the post P up or down. The pressure difference from A to B is the same as that across the diaphragm and is determined by the position of the diaphragm with reference to the orifice in the lower end of the post P. If the pressure in the space H changes slightly because of an irregularity in the action

of the air pump, the pressure in B tends to change likewise so as to alter the pressure difference from A to B across the instrument. The slightest change of pressure in B, however, causes the diaphragm to stretch or contract and hence to further close or open the passage from B to H. As a result, the rate of escape of air from B is not changed appreciably, and consequently the pressure in B is not significantly altered. Actually, the weave of pressure in B about the equilibrium position is so small and so rapid that no change can be detected in the manometers except when a very large amount of air is passing through the regulator. When some of the most permeable materials are being tested a very small pulsation can be observed in the manometer levels. Another regulator exactly like the one shown in detail, except for the addition of a needle valve V through which a certain amount of air can be admitted directly from the atmosphere, is placed in the line just ahead of the air pump. Since the air pump operates at a practically constant capacity, this needle valve is used to by-pass varying amounts of air through the pump, the quantity

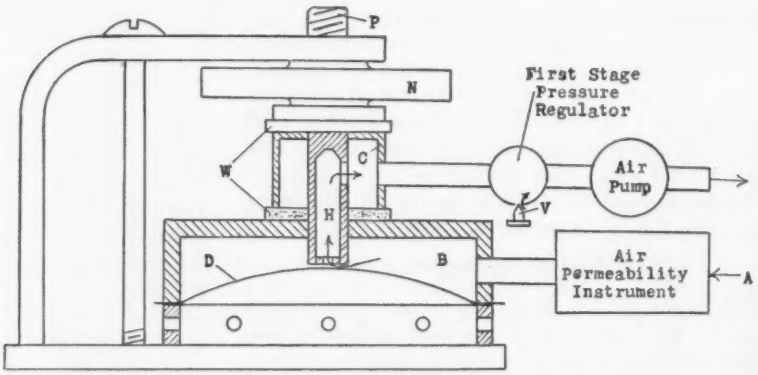

FIGURE 6.—*Pressure regulator for controlling the pressure drop across the instrument.*

depending upon the amount drawn through the instrument. The first-stage regulator (R_1 in figs. 1 and 2) is adjusted for a somewhat greater pressure difference than that desired across the instrument and serves to iron out most of the irregularities before the exact adjustment is made by R_2.

For the protection of the instrument when it is not in use the front is inclosed by folding panels, and the cell is protected from dust by a removable cover O (fig. 2).

2. CALIBRATION OF INSTRUMENT

We have seen from figure 3 that the volume of air flowing per unit time through the specimen under a pressure difference $d=\rho h$, where h is the pressure head across the specimen and ρ is the density of the manometer liquid, is the same as the volume ϕ flowing per unit time through the capillary tube under a pressure head H. Since we have chosen to measure ϕ under the pressure at the inlet side of the capillary we should also measure the volume passing through the specimen under the pressure B on the inlet side of the specimen. If we let V be this volume per unit time, then by Boyle's law $V=\phi\frac{B-d}{B}$. The

volume ϕ corresponding to H is known from the calibration of the capillary, but it is more convenient to have the ratio of ϕ to the corresponding pressure difference tabulated against H, since this ratio is nearly constant for long capillary tubes and hence the interpolations are very simple. It is also convenient to use the ratio of the two pressure heads. The above equation can, therefore, be written:

$$V=\frac{H}{h}\cdot\frac{\phi}{\rho H}\cdot\frac{B-d}{B}\cdot d \tag{1}$$

For values of B within 10 percent of the standard barometric pressure, and d not exceeding 10 g/cm², the value of $\frac{B-d}{B}$ will not differ from unity by more than 1 percent [2] and will not differ by more than 0.1 percent from $1-0.001\ \rho h$. Hence equation 1 may be written in the form

$$\frac{V}{Sd}=\frac{H}{h}\cdot\frac{\phi}{\rho HS}(1-0.001\ \rho h)$$

$$=\frac{H}{h}(1-0.001\ \rho h)\ C \tag{2}$$

in which S is the effective area of the specimen exposed in the air stream. Although ρ and S are constants of the instrument, the quantity $C=\frac{\phi}{\rho HS}$ is not a constant for a given capillary, but varies somewhat with the pressure difference. The coefficients C have been determined as a function of the pressure head from the calibration of each capillary tube with a primary form of gas meter. The air permeability of a material can, therefore, be determined by substituting in equation 2 the value of the coefficient C for the capillary used corresponding to the pressure head H, H and h being readings in centimeters taken directly from the instrument manometers and $1-0.001\ \rho h$ being written down by inspection from the value of h and the constant ρ. If ϕ is expressed in cm³/sec, ρH in g/cm², and S in m², equation 2 evaluates the air permeability in cubic centimeters per second per square meter of material for a pressure difference of one gram per square centimeter [3] (cm³/sec/m²/g/cm²). It turns out that, since S is about 0.01 m², the values of C for all four capillaries are greater than unity.

The capillaries were calibrated in place in the instrument, first by a direct method and then by an indirect method. By the direct method, all except the smallest were calibrated by means of a wet meter having a capacity of 0.1 cubic foot per revolution. An accuracy of about 0.2 percent is possible in the measurement of the rate of discharge of a gas with such a meter (29). The calibrating apparatus was arranged in the following order: Atmospheric pressure→capillary→gas meter→pressure regulators→air pump. The apparatus was tested for leaks at frequent intervals. All calibrations were made in the standard

[2] Since the variation in air permeability of paper is considerably more than 1 percent, $\frac{H}{h}\cdot C$ in equation 2 represents the value of $\frac{V}{Sd}$ sufficiently well for ordinary testing.

[3] The validity of considering $\frac{V}{Sd}$ constant for a given specimen is demonstrated within specified limits in the second publication referred to in the introduction.

atmosphere of 65 percent relative humidity and 21 degrees Centigrade. The gas meter was calibrated at intervals during the calibration of the capillaries by the aspirator-bottle method recommended by Waidner and Mueller (29). The stop watch used was also calibrated and the corrections applied to the data. The meter readings were made in multiples of one complete revolution, and the corresponding time interval varied from 3 minutes to 2½ hours. The capacity of the least capillary was too small to make feasible its calibration by means of the wet meter. Instead, air was drawn through this capillary by allowing water to flow out of a 200-ml pipette connected to one end of the capillary. As a means of overcoming the pulsation arising from the dropwise flow, the water was led off from the discharge tip for a little distance in an inclined trough. As a means of keeping the pressure head constant, the discharge tip was held at a fixed level while the pipette, connected to it with rubber tubing, was moved vertically with a screw mechanism. The fall in the water level inside the pipette was compensated for by the continuous elevation of the pipette at a suitable rate. The water discharged was caught in a weighing can and weighed on a chemical balance. The resulting weight divided by the density of water at the temperature of the experiment gave the volume of air (measured at the pressure within the pipette) which was drawn through the capillary in a given time and at a given pressure difference across the capillary. In all the calibrations, the measured volume was corrected to the inlet pressure of the capillary. Determinations were made at pressure-head intervals of about 2 centimeters on the manometer scale of the flow meter. For each capillary, the values for the capillary coefficients were plotted against the corresponding pressure heads and a smooth curve was drawn among the points. For the two smaller capillaries this was a straight line. With very few exceptions, the points all lay within 0.2 percent of the curve for each of the four sets of data.

The calibration of a set of capillaries by the foregoing method is very tedious and time consuming. As a convenient means of corroborating the calibration occasionally, and of calibrating replacement capillaries, the standardizing flow meter shown in figure 7 was made. It is provided with a set of four capillary tubes very similar to those in the air permeability instrument. These capillaries were calibrated over a somewhat greater range of pressure differences than were the first set. They are kept covered and are never used except for their intended purpose. With this standardizing flow meter connected in place of the gas meter in the calibration train, the capillaries in the air permeability apparatus were again calibrated by this indirect means. The time was, of course, reduced to a small fraction of that required in the calibration by the direct method. The calibrations by the direct and the indirect methods agreed to within about 0.3 percent except for the largest capillary, for which the agreement was within 0.5 percent.

In table 1 are shown coefficients for the four capillaries corresponding to a few values of the pressure difference. The calibration data for the smallest capillary agree very closely with the theoretical flow of a gas through a long capillary tube, but the agreement for the other three capillaries is less and less satisfactory as the capacity of the capillaries increases. If, instead of experimentally standardizing the capillaries, we should adopt the customary procedure (8, 9, 11)

of calculating the theoretical constant[4] of each capillary from its dimensions and using these values in evaluating the air permeability of paper, we should introduce errors ranging from zero to nearly 50 percent, depending upon the capillary used and the pressure difference.

TABLE 1.—*Capillary coefficients for the 4 capillaries of the air permeability instrument at various values of the pressure difference*

Pressure difference	Coefficients C for capillary—			
	C-1	C-2	C-3	C-4
g/cm^2				
5	1.252	10.31	94.1	749
10	1.249	10.19	88.2	690
15	1.245	10.07	83.3	644
20	1.242	9.95	79.5	606
25	1.239	9.84	76.2	571

As confirmation of the continuity of the calibration from one capillary to the next, air permeability tests were made on 16 papers and boards in the 3 transition intervals of the 4 capillaries, an identical area being tested in each case with each of 2 successive capillaries. In nearly all cases the two values thus determined for each material agreed within 0.5 percent. This procedure of making overlapping tests on an identical area of a given material by means of consecutive capillaries is a simple and excellent means of periodically testing the capillaries for accidental fouling that might change the calibration. It dispenses with the necessity for recalibration except when positive evidence of the need is indicated.

For convenience in calculating the results of air permeability tests, complete tables have been prepared from the calibration data which give, for each capillary, the coefficients corresponding to the pressure heads. These tables are, of course, applicable only for a particular density of the manometer liquid and a particular test area of the permeability cell.

TABLE 2.—*Air permeability data illustrating the precision and range of the instrument*

Kind of material	Thickness	Air permeability (in $cm^3/sec/m^2/g/cm$)[4]		
		a	*b*	Difference
	mm			*Percent*
Filter paper	0.25	10,330	10,290	−0.4
Insulating board	11.20	2,564	2,558	−.2
Blotting paper	.50	2,226	2,220	−.3
Newsprint paper	.10	351	349	−.6
Antique book paper	.15	151.1	151.0	−.1
Lined strawboard	1.10	118.7	119.1	+.3
Supercalendered book paper	.05	86.9	86.9	.0
Tagboard	.25	29.80	29.82	+.1
Bond paper	.10	10.42	10.37	−.5
Railroad board	.45	2.097	2.100	+.1
Solid binders board	2.20	1.595	1.596	+.1
Pressboard	.35	.1501	.1512	+.7
Vegetable parchment	.10	.013	.014	+7.7

[4] This dimensional constant, divided by the coefficient of viscosity of air, is the limiting value, as the pressure difference approaches zero, of the coefficients in table 1 for each capillary, and hence can be determined also by the extrapolation of these values to zero pressure difference.

3. PERFORMANCE CHARACTERISTICS

(a) PRECISION

The data in columns *a* and *b* in table 2 represent successive tests made on an identical area of a given specimen, and are typical of a great many tests thus made. In the interim between the two tests on each material, the specimen was removed from the tester and the adjustments of the instrument were upset. Most of the data in table 2 have been chosen from results obtained under very exacting conditions, and illustrate other characteristics in addition to precision. In some cases other tests were made during the interim; in some, a day elapsed between the two tests, the specimens being sealed in an airtight package during the interim to prevent appreciable change in the moisture content; some of the stiffer materials were tested first with the supporting ring referred to in a previous section, and then without it; the edges of some of the specimens were dipped in melted wax in the interim between the two tests, and represent a large class of materials referred to in a succeeding section; some specimens were turned upside down for the second test so as to reverse the direction of flow of air, a particularly good example being the lined strawboard which is the most "two-sided" material listed in the table. The agreement of the two results on each specimen is within a few tenths of 1 percent, except for the last entry, the vegetable parchment, which is far beyond the range for which the instrument was designed.

TABLE 3.—*Data illustrating the variation in the air permeability of different sheets from the same sample*

Kind of material	Air permeability (in $cm^3/sec/m^2/g/cm^2$) of sheet number—				
	1	2	3	4	5
Bond paper	10.98	11.30	11.80	12.33	12.59
Do	206.1	252.1	314.7	355.6	401.9
Ledger paper	24.2	32.0	38.9	47.0	56.0
Map paper	6.41	8.31	9.26	12.05	14.07
Strawboard	160.6	167.5	173.2	176.2	197.1

In contrast with the precision of the instrument, the variability in the air permeability of paper is considerable. Table 3 shows the air permeability values for five sheets taken from each of several samples of paper and board. The variation may be as little as 5 or 10 percent, but it is not unusual to find more than 100 percent spread between the high and low values in a number of sheets from the same sample.[5]

(b) ACCURACY

It has already been pointed out that an accuracy of about 0.2 percent is possible in the calibration method used, and that the agreement in the calibration data by the two methods used was in most cases within 0.3 percent. Experiments in which the menisci of the manometer connecting the inner and the annular cells were

[5] The inherent variability in structure thus indicated is probably the largest factor in the variable nature of the data commonly found in testing the physical properties of paper, which is more often blamed on the inadequacy of the method than on the circumstance that we probably do not test enough of the material to fairly sample it.

adjusted to slightly different levels indicated that the edge-leakage error is probably not greater than 0.3 percent when the test is properly made. Experiments which will be discussed in detail in a succeeding paper indicated that the uncertainty in the effective area exposed to the air stream is probably not greater than 0.5 percent. The readings of the pressure heads are made with an uncertainty of fewer than 5 parts per 1,000. The value for the density of the manometer liquid, the values of the factor $\frac{B-d}{B}$ in equation 1, and the tabulated capillary coefficients are expressed within 0.1 or 0.2 percent of the calculated values. The air permeability values obtained with the instrument may, therefore, be conservatively estimated to be within 1 or 2 percent of the true values.

(c) RAPIDITY

Although time saving is not a primary consideration in precise work, it is a desideratum. In contrast with methods employing the principle of the measuring flask, the character of the paper does not influence very much the time required to complete a test with the new instrument. In most cases it is not necessary to consume time in cutting or specially shaping the specimen. After the adjustments have been made, it is necessary to wait only long enough for pressure equilibrium to be established before the readings are taken, the required time being from a few seconds to perhaps 2 or 3 minutes.

(d) RANGE

The air permeability values in table 2 cover a millionfold range. With the exception of the most impermeable types and possibly a few extremely permeable ones, which require very low scale readings, practically all papers and fibers boards can be tested for air permeability with a reproductibility within less than 1 percent.

4. SPECIAL PRECAUTION IN TESTING THICK, LAMINATED MATERIALS

There are certain kinds of materials which are built up in layers, permitting air to travel laterally between the layers with far greater ease than through the layers. The new design of permeability cell may be suspected of inability to prevent entirely the leakage of air through the edges and between the layers of such materials into the inner cell, unless the annular guard cell were made inconveniently wide. The chance of error is greatest for laminated boards of low permeability, especially if a relatively porous core separates dense surface layers. When such materials are tested, the edges must be dipped in melted wax or otherwise sealed. The wax seal should extend a little distance into the annular cell. To prove that this seal entirely corrects the leakage error, experiments were made with an extreme case of two sheets of paper superimposed and tested, first with free edges, and then with the edges sealed with melted wax. The two sheets were also tested separately. If a and b are the air permeability values of the two sheets tested separately, the air permeability of the two superimposed should be $\frac{ab}{a+b}$. The results in table 4 show that the error resulting from edge leakage in a laminated material may sometimes be considerable, and that it can

be eliminated by sealing the edges in the manner described. Any material having a thickness approaching the width of the guard cell is likely to give trouble unless the edges are sealed. A very large variety of papers and boards were tested both with and without the wax edge seal, and it was found that none of the papers and very few of the boards required the seal. A piece of leather an eighth of an inch thick showed no difference in air permeability when the edges were left free and when they were sealed. A piece of insulating board (not laminated) half an inch thick did, however, show a difference of about 4 percent.

TABLE 4.—*Data showing the necessity of sealing the edges of certain laminated materials*

Kind of material	Air permeability in $cm^3/sec/m^2/g/cm^2$					
	Separate sheets		Superimposed sheets			
	a	b	Calculated $\frac{ab}{a+b}$	Tested with sealed edges	Tested with free edges	Error without seal
						Percent
Bond paper	5.77	6.32	3.017	3.022	3.628	20.0
Ledger paper	5.18	5.31	2.621	2.619	2.767	5.7
Wall board				0.943	1.080	14.5
Binders board				.771	0.931	20.8

5. APPLICATIONS AND LIMITATIONS OF NEW INSTRUMENT

The immediate goal in the development of the new instrument was the study of experimental variables in the measurement of the air permeability of paper and boards, the bearing of these variables upon the structure of paper as revealed through the application of certain theoretical criteria, and the development of information about these variables which might be used in formulating definitions and a standard testing method. This study has been completed and will be described in a subsequent paper.

In addition to the use of the instrument in routine determinations, such as the testing of materials for conformity to specifications, a number of other uses suggest themselves in connection with paper research. It has several times been suggested that the permeability of paper to various processing liquids that do not materially swell cellulose, such as oils, varnishes, waxes, and waterproofing compounds, could be predicted from an air permeability test. The new instrument affords a precise, nondestructive test that might be useful in correlating variations in the common destructive tests, such as tensile, tearing, folding, with variability in the structure of the sheet. It should also be useful in studying the effect of fabrication variables upon the structure of paper, and might turn out to be a valuable control test. Experience with the instrument during the past 2 years indicates that it might be a useful tool in the study of the aging of paper. It holds considerable possibilities in the further study of the structure of paper.

It happens, according to data published by Bergmann and Ludewig (5), that the air permeability of leather lies in practically the

same range as that of paper and fiber boards, and doubtless this material could be precisely measured with the new instrument without modification.

As the last entry in table 2 indicates, there are certain sheet materials generally classified in the category of paper which are below the range of precise measurement with the instrument which has been described in this paper. The problem can best be visualized by reference to figure 8. Three sections of the Bureau of Standards have developed permeability measuring instruments with which air permeability measurements have been made within a range of about 10^{12}. The range of the instruments developed in the textile section (23) and the paper section overlap slightly, so that it is possible to make reliable measurements throughout the regions C and D; but between the ranges which have been covered by the instruments developed in the gas chemistry section (10) and the paper section there is a considerable region which is largely unexplored, and for which there is apparently no instrument of suitable design. This region includes a group of semi-papers and pseudo-papers that are usually classified with paper, such as asphalt saturated

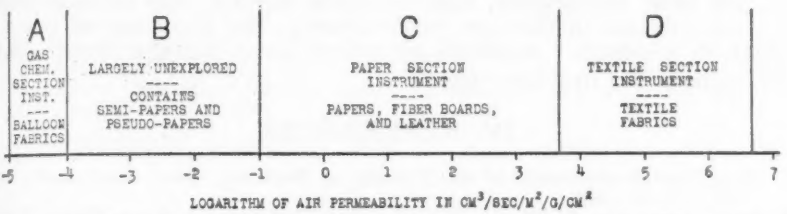

FIGURE 8.—*Chart illustrating the range of measurements which have been reported for the air permeability of sheet materials, the range covered by the new instrument, and the region which yet remains to be explored.*

papers, asphalt films supported between layers of paper, metal foil between layers of paper, vegetable parchment, glassine, cellophane, and thin films of cellulose nitrate and of cellulose acetate. This region is of considerable interest, not only because of the practical significance of permeability of the materials in this range, but also because the nature of results reported for the behavior of materials at the upper and lower limits of the region indicate a transition in the mechanism of transpiration of gases within this range. A particularly attractive possibility of an instrument sensitive in this region is provided by the suggestion that the "grease resistance" of food wrappers might be predicted from their air permeability. The present tests for grease resistance are rather unsatisfactory, and it would be a great boon if these tests could be replaced by such a simple and dependable test as that for air permeability. Permeability instruments now in use for paper testing are inadequate to test out the suggestion.

The region B of figure 8 could probably be explored with modified forms of the two instruments which have been used in regions A and C, or by an instrument combining certain features of the two instruments. There appears to be no difficulty in extending the method of measurement with the capillary flow meter down through practically the whole of this region. It is doubtful, however, if it would be sufficient simply to add capillaries of smaller capacity to

the instrument described in this paper. The relative significance of edge leakage becomes so great, as the permeability comes within this range, that an experimental study would be necessary to determine the suitability for region B of the method used in region C to eliminate error from edge leakage. It seems fairly certain, however, that a considerable portion of the region B could be explored with the new instrument with no significant changes in design except to replace manometer N of figure 1 with an inclined manometer, provide greater sensitivity in the valves that control the adjustment of this manometer, and add suitable capillary tubes of small capacity.

In both region B and region C of figure 8 there are papers, such as fruit wrappers and various food wrappings and cartons, for which the permeability to gases other than air is significant. Permeability studies with various gases could probably be made by the further alteration of the instrument so as to provide a gas-tight seal outside the annular cell, a plate with suitable connections (Q in figure 2) to close the top of the clamping ring and permit the circulation of a gas through the space above the paper, and a means of readily sweeping out the instrument with the gas before a test is begun.

These brief suggestions, together with figure 8, will serve to indicate the relation of the new instrument to the problems of permeability as a whole. Applications which have already been made will be discussed in a later paper.

IV. REFERENCES

1. Barr, The Measurement of the Porosity of Textiles. Jour. Text. Inst., vol. 23, p. 206, 1932.
2. Bekk, Apparatus for Measuring Smoothness of Paper. Paper Trade Jour., vol. 94 (no. 26), p. 41, June 30, 1932.
3. Benton, Gas Flow Meters for Small Rates of Flow. Jour. Ind. Eng. Chem., vol. 11, p. 623, 1919.
4. Bergmann, The Permeability of Hide and Leather. Jour. Int. Soc. Leather Trade Chem., vol. 12, p. 170, 1928.
5. Bergmann and Ludewig, The Permeability of Hide and Leather to Gases. Jour. Int. Soc. Leather Trade Chem., vol. 13, p. 279, 1929.
6. Buckingham, Notes on Small Flow Meters for Air. B.S. Technologic Papers, vol. 14 (T183), 1920.
7. Carson and Worthington, A Study of Sheathing Papers. B.S. Jour. of Research, vol. 3 (RP85), p. 75, 1929.
8. Doughty, Seborg, and Baird, The Volumetric Composition of Paper, IV: Composition of the Air Fraction; Improved Apparatus and Method for Determining Prosity. Tech. Assoc. Papers, vol. 15, p. 287, 1932; Paper Trade Jour., vol. 94 (TS312), 1932.
9. Edwards, The Air Permeability of Leather. Jour. Int. Soc. Leather Trade Chem., vol. 14, p. 392, 1930.
10. Edwards and Pickering, Permeability of Rubber to Gases. B.S. Scientific Papers, vol. 16, p. 327, 1920.
11. Emanueli, The Emanueli Porosity Tester. Paper Trade Jour., vol. 85 (TS98), 1927.
12. Gallagher, Porosity Testing of Paper. Paper, vol. 33 (no. 22), p. 5, Mar. 20, 1924.
13. Hanson, Permeability Versus Porosity of Paper. Paper, vol. 33 (no. 20), p. 11, Mar. 6, 1924.
14. Herzberg, Papierprufung, 6th ed., p. 215, 1927. Verlag von Julius Springer, Berlin.
15. Ivanov, Determining the Porosity of Paper. Paper Trade Jour., vol. 79 (TS147), 1924.
16. Larson, Nelson, and Braatz, Air Infiltration through Various Types of Wall Construction. Heating, Piping, and Air Conditioning, vol. 2, p. 509, 1930.
17. Lhomme et Argy and Bard, The Porosity of Paper to Air. La Papeterie, vol. 53, p. 1438, 1931; Pulp and Paper (Canada), vol. 33, p. 177, 1932.

18. Marsh, Some Notes on the Permeability of Fabrics to Air. Jour. Text. Inst., vol. 22 (T56), 1931.
19. Meyer, Flow of Gas through Capillary Tubes. Annalen der Physik und Chemie, vol. 127, p. 253, 1866.
20. Potts, The Volumetric Composition of Paper, I: Permeability of Paper to Air. Proc. Tech. Sec. Papermakers' Assoc. Gr. Brit. and Ir., vol. 12, p. 91, 1931; World Paper Trade Rev., vol. 96, p. 1257, 1931.
21. Privett, Permeability Test on Waterproof Boards. World Paper Trade Rev., vol. 96, p. 1436, 1931.
22. Ravizza, The Degree of Porosity of Paper. Paper, vol. 33 (no. 17), p. 14, Feb. 14, 1924.
23. Schiefer and Best, A Portable Instrument for Measuring Air Permeability of Fabrics. B.S. Jour. Research, vol. 6 (RP261), p. 51, 1931.
24. Seborg, Doughty, and Baird, The Volumetric Composition of Paper, V: Composition of the Air Fraction; The Effect of Solid Fraction and Thickness on the Porosity and Air Transmissibility of Simple Papers. Paper Trade Jour., vol. 95 (TS149), 1932.
25. Silvio, The Porosity of Papers. Paper Makers' Mo. Jour., vol. 68, p. 433, 1930; and vol. 69, p. 194, 1931.
26. Sindall, Elementary Manual of Paper Technology, p. 142, 1920. Charles Griffin and Co., London.
27. Stoewer, The Air Permeability of Paper. Wochbl. Papierfabr., vol. 64, p. 57, 1933.
28. U.S. Patent No. 1,538,793.
29. Waidner and Mueller, Industrial Gas Calorimetry. B.S. Technologic Papers, vol. 4 (T36), pp. 23–40, 1914.
30. Whitehead and Greenfield, Capillary Action in Impregnated Paper Insulation. Physics, vol. 3, p. 324, 1932.
31. Wilson and Lines, The Ventilating Properties of Leather. Ind. Eng. Chem., vol. 17, p. 570, 1925.

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EFFECT OF EXPERIMENTAL CONDITIONS ON THE MEASUREMENT OF AIR PERMEABILITY OF PAPER

By F. T. Carson

ABSTRACT

By means of the sensitive instrument recently developed at the Bureau of Standards, a careful study has been made of the relation of the rate of flow of air through paper to the experimental conditions. The results show that with few exceptions the flow of air is proportional to the pressure difference, for small pressure differences; proportional to the time of flow; proportional to the effective area of the specimen; and inversely proportional to the thickness of the material. With the type of measuring instrument used the results do not depend upon the viscosity of the air. The effect of relative humidity is unpredictable. The air permeability of paper was found to increase somewhat with decreasing absolute pressure, an unexpected behavior which may be associated with an elastic expansion of the structure.

Except for the absolute-pressure results, all the data agree remarkably well with Meyer's equation for the flow of a gas through a long capillary tube, and indicate that the air passages in paper behave as if they were a group of capillary tubes having an average length of many times the thickness of the sheet.

A comprehensive definition of air permeability in relation to paper and fiber board is presented, and suggestions are made relative to a standard testing method.

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I. INTRODUCTION

The development of the sensitive air permeability testing instrument illustrated schematically in figure 1 has been described in a previous paper.[1] The new instrument was designed to obtain accurate values for a wide range of materials. An annular cell DD surrounds the permeability cell C and serves to by-pass air that leaks in at the edges of the specimen S. Conditioned air at atmospheric pressure has

[1] B.S.Jour. Research, vol. 12 (RP681), p. 567, 1934.

access to the specimen above both cells. A capillary-tube flow meter, consisting of a number of capillaries A, B, etc., of different capacities and a kerosene manometer M, is connected in series with the cell C. One capillary at a time can be opened to the air stream. The capillaries are calibrated against a standardized meter. A partial vacuum in the instrument is produced by an air pump P, resulting in a pressure drop across the instrument not exceeding about 40 g/cm^2. Specially designed pressure regulators R_1 and R_2 maintain unvarying pressure heads h and H across the specimen and the flow meter during the test. Air is simultaneously drawn from cells C and DD, the relative flow being controlled by valves W and Z until the two menisci in manometer N remain at the same level. With no lateral pressure gradient across the cell boundary E, edge leakage into C is prevented. The volume of air flowing per second under a pressure difference h through that part of S above cell C is known from h and the calibration data of the capillary flow meter. The precision of the instrument is such that results are reproducible within one half of 1 percent.

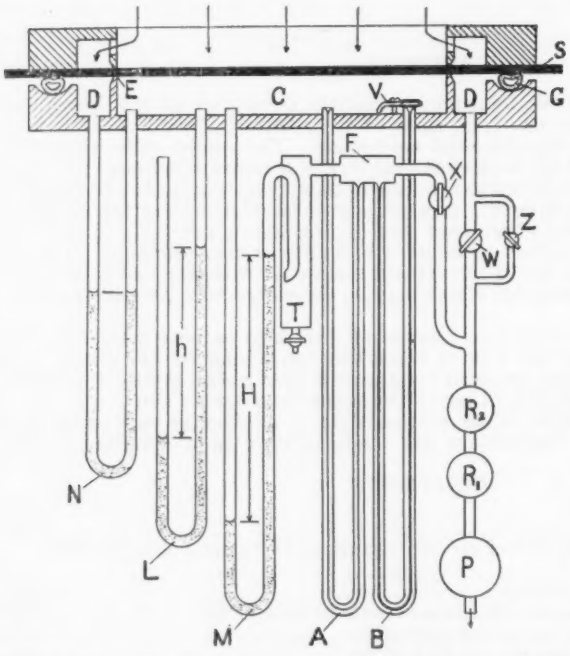

FIGURE 1.—*Schematic drawing of the air permeability instrument used in the investigation.*

A sensitive instrument of this character makes possible the investigation of a number of questions, about which there has been considerable uncertainty arising from differences of opinion of various investigators. One cannot find in the literature satisfactory answers to such questions as the relation of the rate of passage of air through paper to the pressure difference across the sheet; or the relation of this quantity to the area and thickness of the material, and to the temperature and relative humidity of the enveloping atmosphere. A knowledge of these relations is necessary to the very definition of air permeability, and without this knowledge it is impossible to set up adequate standards for air permeability measurements. These relations also give information about the structure of fibrous sheets and the probable nature of the air passages.

II. RELATION OF THE RATE OF FLOW OF AIR THROUGH PAPER TO VARIOUS EXPERIMENTAL CONDITIONS

1. THEORETICAL RELATIONS

The air passages through paper are very small, having cross sections of capillary dimensions. The length of these passages is an unknown quantity; it may be anything from the thickness of the paper to a comparatively lengthy and devious course through the sheet. The cross-sectional contours are irregular in shape and variable in size. Although we do not have equations designed to describe completely the rate of passage of a gas through such a complex structure, we do have, on the one hand, an equation for a straight, tubular capillary the length of which is very great in comparison with the diameter, which is applicable when the flow is streamline; and on the other hand, an equation for the flow of a gas through a nozzle or orifice, which is applicable when the velocity of approach of the gas is small in comparison with the velocity within the orifice. Presumably, within these extremes should be found the essential conditions operative in the passage of air through a sheet of paper.

In the previous publication a simple equation was set down to evaluate the air flow through paper from the data obtained with the new instrument.

$$V = d \cdot \frac{H}{h} \cdot \frac{\phi}{\rho H} \cdot \frac{B-d}{B} \tag{1}$$

For convenience, this equation was also written in another form, applicable within the limits of ordinary laboratory conditions:

$$\frac{V}{Sd} = \frac{H}{h}(1 - 0.001\rho h)\ C \tag{2}$$

In these equations

V = the volume of air, measured at the inlet (atmospheric) pressure B, which, at a given temperature, flows in unit time through the effective area S of paper across which a pressure difference d is maintained,

ϕ = the same volume, measured at the inlet pressure of the capillary,

H = the pressure head across the calibrated capillary tube,

h = the pressure head across the paper,

ρ = the density of the manometer liquid, and

$C = \frac{\phi}{\rho HS}$ · a variable coefficient, corresponding to values of H, obtained from the calibration of the capillary tube and the known value of S.

Equation (1) depends simply upon Boyle's law, and applies, at the temperature of calibration of the capillaries, to any material whatever that can be tested with the instrument.

On the other hand, the equation which, according to Meyer,[2] describes the flow of a gas through the ideal capillary tube may be expressed as follows:

$$\phi P = \phi' p = \frac{\pi r^4 (P^2 - p^2)}{16 l \eta} = \frac{k}{\eta} \cdot D \cdot \frac{2P - D}{2} \tag{3}$$

[2] Annalen der Physik und Chemie, vol. 127, p. 253, 1866.

in which

ϕ = volume of gas, measured at the inlet pressure P, which flows per unit time through the capillary tube,

ϕ' = corresponding volume per unit time measured at the outlet pressure p,

r = radius of the capillary tube,

l = length of the capillary tube,

η = coefficient of viscosity of the gas,

$k = \frac{\pi r^4}{8l}$, a dimensional constant of the capillary tube, and

$D = P - p$, the pressure drop across the capillary tube.

From this equation we may write

$$\frac{\phi}{D} = \frac{k}{\eta} \cdot \frac{2P - D}{2P} \tag{4}$$

Presuming for the moment that the air passages through a sheet of paper behave as if they were a bundle of capillary tubes, we can, by analogy with equation 4, write:

$$\frac{V}{d} = \frac{K}{\eta} \cdot \frac{2B - d}{2B} = \frac{H}{h} \cdot CS \cdot \frac{B - d}{B}, \text{ by equation 1,} \tag{5}$$

in which K is a structural constant of the paper, equivalent to Σk for all the capillary passages involved, and the other symbols have the same significance as in equation 1.

If these air passages behave as capillary tubes, we can make the following deductions from the foregoing equations:

1. The constant $\frac{K}{\eta}$ of equation 5 is the limiting value of $\frac{V}{d}$ as d approaches zero. When d is small in comparison with B, the ratio $\frac{V}{d}$ should be nearly constant (V nearly proportional to d). It is logical that d should be small in the measurement of air permeability, since most uses of paper in which air permeability is significant involve very small values for the pressure drop across the sheet. In the new instrument d does not exceed about 10 g/cm². Hence if d in the expression $\frac{2B - d}{2B}$ were neglected, the result would not be in error by more than 0.5 percent. The equation then becomes equivalent to that of Poiseuille.

2. In the type of measuring instrument used the air flow is affected by the viscosity of the air (a function of the temperature) in the same manner in both the capillary flow meter and the paper, if both are capillary in nature. Now, if equations 4 and 5 represent the behavior of the two elements of the instrument, the division of one by the other gives $\frac{D}{d}\left(=\frac{H}{h}\right)$ independent of η. Hence, for a given pressure difference the value of $\frac{V}{d}$ (corresponding to the temperature of calibration of the capillary) obtained from equation 1 should be independent of the actual temperature at which the paper is tested by means of this double-flow-meter principle.

3. Since, according to equation 3, the rate of flow of air is inversely proportional to the length of a given capillary, $\frac{V}{d}$ should be inversely proportional to the thickness of the sheet if the structure is homogeneous with respect to the thickness dimension.

4. Within experimental error the value of V, for a given value of d, should be independent of the absolute pressure B over the ordinary range of barometric pressures. The calibrations of the capillaries should likewise be independent of the absolute pressure. This relation becomes evident when we substitute different values for P and B in equations 4 and 5 while keeping the pressure difference constant. For a pressure difference not exeeeding 25 g/cm^2, the absolute pressure may differ as much as 10 percent from the standard barometric pressure without altering the rate of air flow by more than about 0.1 percent for a given pressure difference. Although these equations indicate that the volume rate of discharge of air (expressed in terms of the pressure at, say, the inlet end) through a capillary at a given pressure difference is the same for all usual values of absolute pressure, it is curious that some investigators have attempted to correct the indicated volume rate of discharge to what it would be under standard conditions, by a mistaken application of Boyle's law.

If, on the other hand, we consider paper as in effect a sheet perforated by a myriad of small orifices we should expect, according to Buckingham,[3] the following equation to more nearly describe the behavior of air passing through it:

$$\frac{V}{d}=M\sqrt{T}\frac{\sqrt{\left(\frac{B-d}{B}\right)^{\frac{10}{7}}-\left(\frac{B-d}{B}\right)^{\frac{12}{7}}}}{d} \tag{6}$$

in which M is a constant involving the cross sectional areas of the orifices (but not their lengths), T is the absolute temperature, and the other symbols have the same significance as in equation 5. From equation 6 we can then make the following deductions for a sheet perforated by orifices:

1. The ratio $\frac{V}{d}$ should not be constant with changing pressure difference, but should decrease rapidly as d increases. For small values of d it is nearly inversely proportional to the square root of d by equation 6.

2. We find, by dividing equation 6 by equation 4, that $\frac{D}{d}\left(=\frac{H}{h}\right)$ is nearly proportional to the five fourths power of the absolute temperature, for ordinary room temperatures.[4] Hence the value of $\frac{V}{d}$, determined with the new instrument and equation 1, should differ from that corresponding to the temperature of calibration of the capillary by nearly one half percent for each degree C by which the testing temperature differs from the temperature of calibration.

[3] B.S.Technologic Papers, vol. 14, (no. 183), 1920.

[4] The approximate equation $\eta=\eta_o\left(\frac{T}{273}\right)^{5/4}$ was used to express η in terms of T in equation (4).

3. Since M does not depend upon the length of the nozzles or orifices, the value of $\frac{V}{d}$ should be independent of the thickness of the sheet.

4. For a constant pressure difference the rate of passage of air through such a sheet should increase with decreasing absolute pressure. For example, the value of $\frac{V}{d}$ at standard barometric pressure is increased by about 5 percent, according to equation 6, when the barometric pressure is reduced 10 percent.

The duration of the test and the area of the specimen are also implicitly involved in equations 5 and 6, but a given change in either one of these quantities should affect the results in a like manner, whether the air passages behave as capillaries or as orifices, provided the material is homogeneous with respect to area and is not altered in structure by the testing conditions. Although the effects of varying these quantities in air permeability tests are not useful as criteria of the nature of the air passages, these variables will be treated along with the other experimental conditions because of their importance in the development of standards for air permeability measurements and because investigators do not agree as to their effects on the measurements.

The foregoing criteria for the nature of the structure of paper may be summarized as follows:

If the air passages behave as capillary tubes, $\frac{V}{d}$ should be constant with change in pressure difference, constant with change in temperature, inversely proportional to thickness, constant with change in absolute pressure.

If the air passages behave as orifices or nozzles, $\frac{V}{d}$ should be inversely proportional to the square root of the pressure difference, increase with increasing temperature, constant with change in thickness, increase with decreasing absolute pressure.

In the application of these criteria to the experimental data it should be emphasized that the values of $\frac{V}{d}$ reported do not depend in any way upon air-flow theory nor upon any assumptions about the nature of the air passages through the material tested, since equation 1 is based simply upon the calibration of the instrument.

2. EFFECT OF PRESSURE DIFFERENCE ON RATE OF FLOW OF AIR

The relation of the pressure difference across the sheet to the rate of flow of air through it is so important to the convenient measurement of air permeability and the expression of the results, and to the translation of the laboratory tests into practical significance, that considerable attention has already been given to the study of this relation. The various reports, however, record a considerable diversity of conclusions. Bergmann and Ludewig,[5] working with leather, reported air flow proportional to the pressure difference, but Edwards,[6] working with the same material, concluded that air flow is not truly proportional

[5] Jour. Int. Soc. Leather Trade Chem., vol. 13, p. 279, 1929.
[6] Jour. Int. Soc. Leather Trade Chem., vol. 14, p. 392, 1930.

to the pressure difference. Schiefer and Best,[7] working with textile fabrics at very low pressure differences, found the two quantities proportional for some fabrics, but not proportional for others. Several investigators have reported results for paper. Lhomme et Argy and Bard[8] reported the air flow proportional to the pressure difference except for condenser paper. Potts[9] concluded that air flow is virtually proportional to the pressure difference, but pointed out that there are exceptions. Silvio[10] at first reported the two quantities proportional, except for thin papers or papers of poor formation, and later concluded that air flow is proportional to the 0.925 power of the pressure difference. Stoewer[11] found the two quantities proportional, but an anonymous investigator,[12] replying to Stoewer, reported not even a semblance of proportionality between pressure difference and the rate of passage of air through paper.

A great many tests have been made with the precision air permeability tester to show, for various kinds of papers and fiber boards, the relation between the pressure difference and the volume of air transmitted per unit time. The value for $\frac{V}{d}\times 100$ are recorded in table 1 for values of the pressure difference between 0 and 12 g/cm^2.

TABLE 1.—*Data showing the relation of air transmission to the pressure difference across the sheet*

Kind of material	Thickness	Ratio of air transmission to pressure difference for pressure differences of—					Difference, first and last columns
		0 to 4 g/cm^2	4 to 6 g/cm^2	6 to 8 g/cm^2	8 to 10 g/cm^2	10 to 12 g/cm^2	
	mm	*100 V/d*	*100 V/d*	*100 V/d*	*100 V/d*	*100 V/d*	*Percent*
Binders board	2.30	1.434	1.430	1.430	1.432	1.429	0.4
Lined board	1.10	57.3	57.2	57.3	57.5	57.5	.4
Strawboard	.95	198.9	198.4	198.8	199.0	197.9	.5
Tag board	.40	118.9	118.6	118.7	118.3	118.3	.5
Parchment deed	.165	2.097	2.098	2.103	2.092	2.084	.6
Machine-finished book	.140	49.05	48.74	48.87	48.85	48.80	.5
Wrapping (no. 2 Kraft)	.125	269.3	269.2	269.1	267.8	267.4	.7
Bond	.115	11.32	11.35	11.30	11.32	11.28	.4
Coated book	.090	6.82	6.81	6.81	6.88	6.82	.0
Machine-finished book	.090	171.2	171.2	170.8	171.2	171.4	.1
Newsprint	.080	517	516	515	514	511	1.2
Supercalendered book	.075	31.17	31.30	31.28	31.07	31.10	.2
Map paper	.065	10.65	10.62	10.62	10.58	10.56	.8
Manifold tissue	.065	64.4	53.2	49.3	44.5	40.7	36.8
Stereotype tissue	.040	27.42	26.22	25.79	25.47	24.88	9.3
Glassine	.040	1.668	1.558	1.503	1.466	1.412	15.4

The values in each vertical column were determined at some pressure difference within the pressure range designated at the top of that column.

With the exception of a few of the thinnest papers, the rate of flow of air through the paper is proportional to the pressure difference to within a fraction of 1 percent. These data agree remarkably well with the relation predicted by equation 5 for a capillary-tube structure of paper. In all the tests that have been made the only exceptions

[7] B. S. Jour. Research, vol. 6, (RP261), p. 51, 1931.
[8] La Papeterie, vol. 53, p. 1438, 1931; Pulp and Paper (Canada), vol. 33, p. 177, 1932.
[9] Proc. Tech. Sec. Papermakers' Assoc. Gr. Brit. and Ir., vol. 12, p. 91, 1931; World Paper Trade Rev., vol. 96, p. 1257, 1931.
[10] Paper Makers' Mo. Jour., vol. 68, p. 433, 1930; and vol. 69, p. 194, 1931.
[11] Wochbl. Papierfabr., vol. 64, p. 57, 1933.
[12] Wochbl. Papierfabr., vol. 64, p. 174, 1933.

found have been thin papers of rather poor formation, in most of which numerous "pinholes", or minute orifices, could be seen extending through the sheet. In these exceptional cases the relation of air flow to pressure difference tends in the direction predicted by the equation for an orifice. The criterion for orifice-like behavior, $\frac{V}{\sqrt{d}}$ = a constant, however, is not satisfied in any case met with, a fact which suggests, for these thin, poorly formed papers, a structure intermediate between capillary-like passages and orifices, or a structure made up of both.

3. EFFECT OF TIME ON RATE OF FLOW OF AIR

Stoewer [13] has presented data to show that the air permeability of paper is a function of the time the paper is exposed in the air stream, and concludes that the pressure difference across the sheet produces a progressive change in the density of the fibrous structure. Although such an effect might result from excessive pressure differences, no evidence of such an effect has been observed within the range of pressure differences used in this investigation. It will be recalled that when the precision of the new instrument was being studied, it was found that successive tests made on a given specimen under carefully controlled conditions agreed within a few tenths of 1 percent. Further evidence is afforded by the data in table 1. The several values for each material represent varying periods of exposure in the air stream, since all were obtained on the same specimen by successive adjustments of the pressure difference. The time period for each material was about the same as that in Stoewer's experiments.

Although the rate of passage of air through a given structure under given testing conditions is constant with time, the structure may change over a period of time. For example, many instances have been observed in which the air permeability of a specimen was altered after it had gone through a cycle of hygrometric changes, as will later be seen when the effect of humidity is discussed. Such an effect is evidently brought about by changes in the structural relations of the fibers as they absorb moisture and swell, or give up moisture and shrink. An unusual instance has been observed in which the air permeability of a specimen increased tenfold after it had been stored for a year subject to hygrometric changes indoors. Other specimens stored under the same conditions changed very little.

4. EFFECT OF AREA ON RATE OF FLOW OF AIR

Most investigators have assumed that the quantity of air flowing through paper in a given time is proportional to the area exposed in the permeability cell of the testing instrument. Hanson,[14] however, has presented data indicating that the rate of flow is not proportional to the area exposed. His data show air transmission values in the ratio of 1 to 3.2 for areas in the ratio of 1 to 4. He presumed a sufficient distortion of the structure, resulting from the clamping pressure at the boundary of the cell, to account for the discrepancy. The investigation of such a boundary effect, or other contributing factors inherent in the testing method, is complicated by the variability of paper and fiber boards. This difficulty has not arisen in the study of

[13] See footnote 11.
[14] Paper, vol. 33, no. 20, p. 11, Mar. 6, 1924.

other variables because the tests can be made on an identical area of material.

It must be evident, upon reflection, that we do not know what the effective area is when there is a horizontal pressure gradient in the annular area between the clamping rings of the permeability cell. Some air must pass through the structure of the paper in this region, making the effective area greater than the nominal area bounded by the clamping rings. We are not justified, therefore, in concluding with Hanson that the quantity of air transmitted is not proportional to the area exposed to the air stream, because we do not know what this area is. Moreover, we are forced to the conclusion that in none of the twenty-odd designs of air permeability apparatus described in the literature is the test area known except approximately. Even when the sheet is clamped between rubber rings and sealed at the edges there must be some movement of air within the structure lying between the clamping rings.

It will be recalled that in the instrument shown in figure 1 the test area is bounded by a narrow ring of metal, and that the pressure drop through the sheet is precisely the same on both sides of this bounding ring. Hence the uncertainty in the test area is not greater than half the contact area of this ring with the material. If the ring is made very narrow and the test area large (since the ratio of periphery to area decreases as the area increases), the uncertainty in effective area can be made very small, but of course never zero. Is the effective area determined by the inside diameter of the bounding ring, by the mean diameter, or by some intermediate value? It is unlikely that it is represented by the inside diameter, since it has been observed that the quantity of air transmitted is decreased slightly by an increase in the clamping pressure. For example, the decrease in air transmitted was found to vary from a negligibly small amount for a thin, hard paper, to about three fourths of 1 percent for a thick, compressible material, when tests were made with a cell in which the contact area of the ring was about 1.5 percent of the test area, and the clamping pressure was varied from that just sufficient to make the balancing manometer function properly, to a pressure sufficient to indent the material.

In order that the effect of area might be studied, another permeability cell was made having an area approximately one tenth that of the original cell. A sheet was first tested in the large cell; then, within the area thus tested, seven tests were made with the small cell, the seven tests being symmetrically distributed so as to fairly sample the area tested in the large cell. Finally the whole area was again tested in the large cell. The average of the two tests with the large cell (which, for most of the materials tested, agreed to within about 0.3 percent) was then compared with the average of the seven made with the small cell. Although the materials for these tests were selected for uniformity rather than for variety, they represent considerable differences in characteristics which might be presumed to enter into the case. An antique book paper and a supercalendered book paper were selected for their widely different surface characteristics. The strawboard selected is thick and compressible in comparison with the bond paper, and its air permeability per unit thickness is more than a hundred times as great as that of the bond paper. When the results were calculated on the basis of the free area repre-

sented by the inner diameter of the clamping rings there was a discrepancy of 3 percent or more, as shown by table 2. When, however, they were calculated on the basis of the area represented by the mean diameter they were found to be in good agreement. The agreement is, on the whole, so good that we may conclude with confidence that the effective area is sufficiently well represented by the area enclosed within the median circle defined by the average diameter of the bounding ring, and that the quantity of air transmitted is proportional to this area for otherwise identical conditions.

TABLE 2.—*Data showing the relation of the area of the sheet exposed in the air stream to the amount of air transmitted through it in a given time*

Kind of material	Ratio of air transmitted to area exposed for—					
	Nominal areas [1]—			Effective areas [2]—		
	100 cm²	10 cm²	Difference	100.8 cm²	10.4 cm²	Difference
			Percent			*Percent*
Bond paper 1	11.27	11.68	+3.6	11.18	11.23	+0.5
Bond paper 2	11.75	12.11	+3.1	11.65	11.64	−.1
Bond paper 3	10.50	10.86	+3.4	10.41	10.44	+.3
Bond paper 4	11.88	12.32	+3.7	11.78	11.84	+.5
Strawboard 1	198.8	204.3	+2.8	197.2	196.4	−.4
Strawboard 2	175.2	180.6	+3.1	173.7	173.6	−.1
Antique book paper	151.2	156.3	+3.4	149.8	150.2	+.3
Supercalendered book paper	88.6	91.8	+3.6	87.8	88.3	+.6

[1] Area of cell aperture.
[2] Area determined by the mean diameter of the bounding ring.

5. EFFECT OF TEMPERATURE ON AIR PERMEABILITY

Measurements were made of the flow of air through papers, fiber boards, and glass capillaries at a relative humidity of 65 percent and at temperatures of 27 C and 21.5 C. According to conclusions reached in the section on theoretical relations, this difference in temperature should make no difference in the measurements if we are dealing with capillary phenomena in both the material tested and the capillary flow meter with which we measure the air flow. On the other hand, if the air passages in paper behave as orifices, we should expect the results at the higher temperature to be 2 or 3 percent higher than those at the lower temperature. The results of the measurements for 10 papers and fiber boards, in the order of decreasing air permeability, are shown in table 3. These data indicate that for ordinary room temperatures, the results by this method of measurement are practically independent of the temperature. This is not true for any of the displacement methods. Similar measurements for two capillary tubes at several values for the pressure difference are also shown in the table, being expressed as the ratio of air flow to pressure difference. These results do not, of course, imply that the actual amount of air going through the sheets or the capillary tubes at the two temperatures was not different, but that in each case the result obtained is the air permeability at the temperature of calibration of the flow meter. The agreement in results at different temperatures in table 3 is further evidence that the equation for flow through a capillary applies to paper and fiber boards, and hence that the air passages through them are capillary in nature.

TABLE 3.—*Air permeability measurements at different temperatures*

Kind of material	Air permeability		
	Tested at		Difference
	21.5 C	27 C	
	$cm^3/sec/m^2/g/cm^3$	$cm^3/sec/m^2/g/cm^3$	*Percent*
Mimeograph paper	282.8	281.3	−0.5
Strawboard	177.0	175.9	−.6
Antique book paper	151.1	151.0	−.1
Lined strawboard	128.7	128.0	−.5
Supercalendered book paper	86.9	86.9	.0
Sulphite manila tagboard	29.81	29.82	.0
Rag index paper	11.28	11.29	+.1
Coated book paper	10.18	10.29	+1.1
Sulphite index paper	8.69	8.68	−.1
Railroad board	2.56	2.58	+.8
Capillaries	$100V/d$	$100V/d$	
Capillary A (d=24)	1.237	1.238	+.1
Capillary A (d=16)	1.241	1.241	.0
Capillary A (d=11)	1.247	1.244	−.2
Capillary B (d=26)	8.98	8.95	−.3
Capillary B (d=18)	9.13	9.12	−.1
Capillary B (d=6)	9.38	9.36	−.2

A very important requisite in these tests was the protection of the materials from a change in equilibrium moisture content during the interim between tests at the two temperatures, for otherwise a slight change in structure might ensue. During the interim the materials were kept in an airtight package. Preliminary experiments in which this precaution was not taken were inconclusive.

6. EFFECT OF RELATIVE HUMIDITY ON AIR PERMEABILITY

The theoretical relations which we have considered do not give us any clue as to what effect the relative humidity of the air might be expected to have on the rate of flow through minute passages, except for the change in the viscosity of the air; and it has just been seen that a change in viscosity (a function of temperature) will not affect the results. There are certain characteristics of minute passages, however, which lead us to suspect the influence of relative humidity. Very small capillaries are prone to condense water vapor. Obstruction of this nature might be serious at high relative humidities. We should expect this difficulty, if any, with fine glass capillaries used as standards. Tests were made of the behavior of the two capillary tubes in the instrument having the smallest bores, at relative humidities of 65 percent and below. There was no evidence of fouling by condensation at these humidities.

In the case of paper, we should expect in addition a change in the structure of the sheet to result from the exposure to atmospheres of different relative humidity. The walls of the fibers take up moisture and swell as the relative humidity is increased. This swelling probably increases the size of passages within fibers, but may either increase or decrease the size of passages between fibers, depending upon conditions within the structure. Although we should expect a

change in relative humidity to affect the air permeability of paper, we are unable to predict either the magnitude or the direction of this effect. Gallagher,[15] Hanson,[16] and L'homme et Argy and Bard [17] found little or no effect of changing relative humidity on the air permeability of paper. Herzberg [18] concludes that the swelling of the fibers with increasing relative humidity results in decreasing the air permeability of paper. Stoewer [19] presented data to show that papers made with little beating increase considerably in air permeability with increasing relative humidity, but that papers made of well-beaten stock decrease somewhat in air permeability with increasing relative humidity.

The same 10 materials appearing in table 3 were tested at a constant temperature and at relative humidities of 45, 55, and 65 percent, and finally again at 45 percent. An identical area of each sample was tested throughout to eliminate the effect of the inherent variability of the material, as has been done in all these studies whenever possible. During the interval between successive exposures and tests under different conditions the specimens were sealed in an airtight receptacle with relatively little free space, so that the moisture content of the specimens could not change appreciably. Under these carefully controlled, though limited range of conditions, appreciable effects of the humidity of the air on air permeability were found. But some materials increased while others decreased in air permeability for a given change in humidity. The largest change noted, however, was less than 4 percent. Two other sets of the same materials were tested over a wider humidity range, although the lower humidities were not under exact control, advantage simply being taken of low humidities in the laboratory on cold, dry winter days. One set was tested first at 10 and then at 65 percent relative humidity. The other set of samples was tested first at 25, then at 65, then at 10, and finally again at 65 percent relative humidity. The results for the three sets of tests are summarized in table 4 as percentage changes in air permeability, for the relative humidity range and direction of change in humidity indicated at the top of each column. The materials are again arranged in descending order of air permeability, just as in table 3.

These data indicate that the air permeability of some materials is very little affected by changes in relative humidity, while that of others may be altered at least as much as 15 percent within the range studied. If the higher range of humidities had been included in the study, considerably greater changes in air permeability might have been found. In general, the behavior of each material is characteristic, although there are some instances of rather erratic change both in direction and magnitude. Certainly, the structure is much less stable with changing relative humidity than with changing temperature when the humidity is constant. It is evident that comparable determinations of the air permeability of paper and boards must be made at a standard relative humidity, since we cannot tell beforehand how a given material will be affected by humidity changes.

[15] Paper, vol. 33, no. 22, p. 5, March 1924.
[16] See footnote 14.
[17] See footnote 8.
[18] Papierprüfung, 6th edition, p. 216, 1927.
[19] See footnote 11.

TABLE 4.—*Data showing the effect of relative humidity on air permeability*

Kind of material	Change in air permeability with change in relative humidity for—				
	First set—	Second set—	Third set—		
	45 to 65% relative humidity	10 to 65% relative humidity	25 to 65% relative humidity	65 to 10— relative humidity	10 to 65% relative humidity
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
Mimeograph paper	−0.3	−0.3	+0.6	+0.6	+0.1
Strawboard	−.2	−2.6	−.2	+1.4	−.7
Antique book paper	−.9	−1.2	−.7	+2.4	−1.6
Lined strawboard	+.2	+1.3	+.7	+1.0	+.5
Supercalendered book paper	+3.5	+11.1	+13.0	−5.3	+11.4
Sulphite manila tagboard	+1.3	+3.4	+4.2	−.6	+3.5
Rag index paper	−2.8	−4.7	+4.8	+12.5	−5.0
Coated book paper	−3.8		−2.8	+14.9	−8.4
Sulphite index paper	+1.5	+7.4	+9.6	+.6	+5.6
Railroad board	−1.6	−8.6	+.1	+12.2	−4.8

7. THICKNESS OF THE SHEET AND AIR PERMEABILITY

For most uses of paper and fiber boards it is not necessary to bring thickness into the expression of the air permeability, since the overall value is the significant quantity. Sometimes, however, it is necessary to determine the porosity of the fibrous structure, as, for example, in paper-making studies involving the choice and treatment of raw materials and the formation of the sheet, and in studies of the relation of the structure of the material to its physical properties. In such studies the air permeability of a unit thickness of the material is of primary interest and presumes a knowledge of the relation between air permeability and thickness. This relation is also of considerable interest because of its bearing upon the nature of the air passages in paper.

From equations 5 and 6 we may infer that the quantity of air passing through paper should vary inversely as some power of the thickness of the sheet, the power being unity if the air passages behave as long capillary tubes, zero if they behave as orifices or nozzles, and somewhere between zero and unity if they have characteristics intermediate between orifices and long capillary tubes.

Emanueli [20] assumed air permeability inversely proportional to thickness and made use of the relation in evaluating his "porosity constant." A few investigators have reported data on this relation, but do not agree in their conclusions. Silvio [21] made up sheets in various thicknesses from a given stock or fiber suspension, presuming the sheets to be alike except for the differences in thickness. After measuring the air permeability of these sheets he came to the somewhat startling conclusion that the volume of air transmitted per unit time, area and pressure difference is practically independent of the thickness except for very thin papers. In accordance with the theoretical criteria which we have discussed, this conclusion would indicate that the air passages behave as orifices for all except very thin papers, which is precisely the opposite of what we have found for all other criteria thus far considered. A somewhat similar finding is

[20] Paper Trade Jour., vol. 85 (TS98), 1927.
[21] See footnote 10.

reported by Seborg, Doughty, and Baird [22] who likewise made up sheets in various thicknesses from a given fiber suspension. These investigators controlled also the solid fraction or apparent density of the sheets, so that their conclusions are all the more puzzling. They concluded that air transmission is nearly independent of thickness for a constant solid fraction, except when the solid fraction is less than 0.4, that is, when the volume of the solid material (fibers) in the sheet is less than 0.4 of the volume of the sheet. For these more porous materials they concluded that air transmission increases with decreasing thickness. Potts [23] used a different method and reached different conclusions. He tested thicker and thicker units built up by placing sheets of paper on top of one another. Using combinations of from 1 to 8 sheets, he came to the conclusion that air transmission is inversely proportional to some power of the thickness. This power was less than one for all the results he reported by this method, and was different for each kind of paper, being smaller for the denser papers. In conclusion, Potts says: "This is experimental proof that the interfiber spaces of paper are not simple capillaries, and that the thickness of the sample should not enter into the expression of permeability until we know more about its meaning." This investigator subsequently reported [24] some tests of sheets made in various thicknesses from a given fiber suspension, according to the procedure of Silvio and of Seborg, Doughty, and Baird. These results correspond to a power greater than unity in Potts' equation, and are in strong contrast to the data of the other investigators who used the same method of attack, but who obtained data corresponding to the zero power of the thickness in the equation.

Both of the methods used by the investigators, whose studies have been summarized above, are somewhat at fault for the purpose of determining the effect of thickness upon air permeability. When sheets are made up in different thicknesses from a given stock there is no assurance that the structural pattern will remain constant. Especially if a hand-sheet machine is used, there is more than a possibility that the orientation of the fibers will change as the thickness of the fiber mat is increased. In fact Seborg, Doughty, and Baird suggest as much in their paper, although they assume an orifice-like mechanism in their perforated-plate analogy. It is conceivable that capillary-like passages of constant length in the different thicknesses of sheets might result from an orientation of the fibers such that they extend from surface to surface in all the sheets. It is difficult to explain otherwise the results obtained by Silvio and by Seborg, Doughty, and Baird. The writer has had an opportunity to test some book papers in different thicknesses, made at the Bureau of Standards on a semicommercial paper machine of the fourdrinier type. These papers were all taken from a single machine run, during which the density was maintained at a nearly constant value while the thickness was varied over nearly a threefold range. The results of these tests, which are shown in table 5, indicate, in contrast with the data reviewed above, that the air permeability is approximately inversely proportional to the thickness of the sheet, except for the very thin sheets. This method of approach may serve very well to explore the possibilities of making paper in different thicknesses so as

[22] Paper Trade Jour., vol. 95 (TS144), 1932.
[23] See footnote 9.
[24] Proc. Tech. Sec., Papermakers' Assoc. Gr. Brit. and Ir., vol. 12, p. 118, 1931.

to have certain characteristics of permeability, but it is inconclusive as a means of finding out how air permeability varies with thickness in a given material.

TABLE 5.—*Data showing the relation of the air permeability to the thickness of sheets of paper made from a given fiber suspension, the density being nearly constant*

Thickness L	Air permeability A	$A \times L$	Density
mm	*cm³/sec/m²/g/cm²*		*g/cm³*
0.085	340.6	29	0.67
.115	322.5	37	.68
.120	350.0	42	.68
.140	300.7	42	.67
.145	293.7	43	.67
.165	254.1	42	.68
.165	259.1	43	.67
.170	292.3	50	.65
.195	230.7	45	.68
.210	210.0	44	.69

The first method used by Potts, in which two or more sheets are tested together, is more suitable, although Potts overlooked some important points in the use of this method of approach. He assumed the air permeability of each sheet in the built-up unit to be the same, and erroneously considered it sufficient to multiply the air permeability figure of this built-up unit by the number of sheets in it, in testing the validity of the inverse proportionality between air permeability and thickness. It is necessary to determine the air permeability of each sheet separately as well as to test them all in combination, and the identical area of each sheet must be exposed in the air stream when the sheets are tested separately and in combination. Although this investigator speaks of precautions to prevent leakage of air between the sheets, his results indicate that he did not prevent this type of leakage. In fact, it is a most difficult thing to do. Even with the instrument used in this investigation, which is designed to prevent a lateral pressure gradient at the cell boundary, it was found necessary, in order to prevent this type of leakage, to seal the edges of the sheets together for a little distance into the annular guard cell. Leakage of air between the sheets at the edges of the permeability cell would account for just the sort of results which Potts obtained: The air transmission decreased less rapidly than the increasing number of sheets would demand, and this tendency became more pronounced as the less permeable types of paper were tested. This type of edge leakage is a far more logical explanation of the type of results obtained than the paradoxical alternative of presuming that the air passages become more and more orifice-like as we deal with papers which are less and less permeable to air.

If two sheets are laid together and tested for air permeability, and if V is the volume of air through a given area in unit time, d the pressure difference across both sheets, d_1 and d_2 the pressure difference across the first and the second sheets, respectively,

$$\frac{V}{d} = \frac{V}{d_1 + d_2} = \frac{\frac{V}{d_1} \cdot \frac{V}{d_2}}{\frac{V}{d_1} + \frac{V}{d_2}} = \frac{ab}{a+b}, \tag{7}$$

in which we let $a=\frac{V}{d_1}$ and $b=\frac{V}{d_2}$. This relation would probably hold regardless of the nature of the air passages, because the sheets are in series with an air space between, in consequence of which the velocity of approach to each sheet is small in comparison with the velocity within the air passages. However, if the air passages behave as a group of capillary tubes, we can evaluate $\frac{V}{d_1}$ and $\frac{V}{d_2}$, notwithstanding the fact that we do not know the values of d_1 and d_2, because, in that case, each of these ratios is constant for all small values of the pressure difference. Hence we can evaluate these quantities by testing the two sheets separately at any convenient, small pressure difference. Equation 7, therefore, is a criterion for the nature of the air passages when two sheets are tested, first separately and then in combination, and when the precautions discussed above are taken to prevent leakage between the sheets. Results obtained in this way are shown in table 6. A more convincing variation on this procedure, which eliminates the air space between the sheets, is effected by wet-pressing the sheets together so as to make a loosely bound unit.

TABLE 6.—*Relation of air permeability to thickness, shown by tests of sheets made separately and in combination*

Kind of paper	Air permeability of sheets tested—			
	Separately		In combination	
	First sheet a	Second sheet b	Calculated $\frac{ab}{a+b}$	Experimental
	$cm^3/sec/m^2/g/cm^2$	$cm^3/sec/m^2/g/cm^2$	$cm^3/sec/m^2/g/cm^2$	$cm^3/sec/m^2/g/cm^2$
Ledger paper	5.175	5.310	2.618	2.619
Bond paper	9.74	10.43	5.040	5.037
Rope manila paper	107.5	109.2	54.20	54.15
Strawboard	183.0	176.5	89.9	89.4
Sheets wet-pressed together				
Writing paper	17.74	17.93	8.92	8.90
Cover paper	202.1	175.3	93.9	93.6

After it is dried and conditioned, this double sheet is tested without the edge seal, and then the two halves are peeled apart and tested separately. The last two papers in table 6 were treated in this manner.

These results clearly indicate that, if we increase the thickness of a sheet without altering any other structural characteristic, the new sheet behaves as if we have joined together capillary tubes, that is, as if we have increased the length of the capillary passages in proportion to the increase in thickness. From these experiments we may conclude that air permeability is inversely proportional to the thickness of the sheet, and that the air passages behave, according to the thickness criterion, as if they were long capillary tubes.

8. EFFECT OF ABSOLUTE PRESSURE ON AIR PERMEABILITY

The effect of the absolute pressure on the air permeability of paper apparently has not figured in the studies of previous investigators reporting in the literature. According to equations 5 and 6, we should expect a change in absolute pressure (within usual limits) to have practically no effect on the air permeability of paper if the air passages behave as capillary tubes, but to have a significant effect if they behave as orifices.

Air flow measurements through capillary tubes and through paper were made with a calibrated capillary flow meter at various values of the absolute pressure between one atmosphere and about nine tenths atmosphere. The apparatus used is shown in figure 2. The reduction in absolute pressure on the inlet side of the test piece was obtained by attaching a small capillary tube R to the inlet of the test piece so

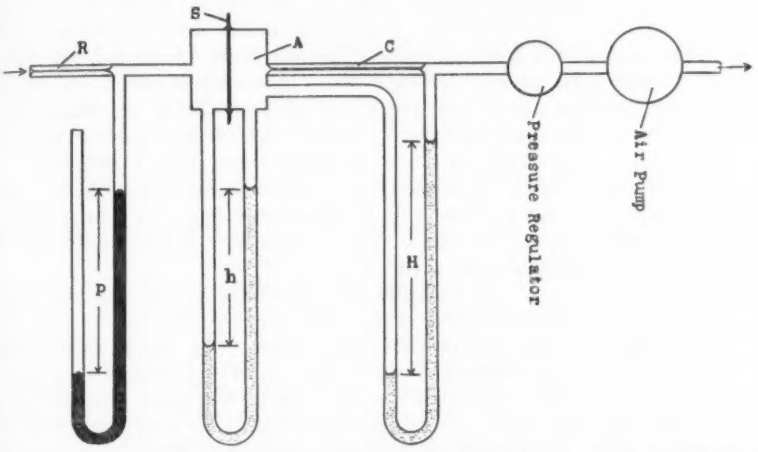

FIGURE 2.—*Apparatus used in experiments at different absolute pressures*

that the required pressure drop p would take place through this capillary. A mercury manometer was used to measure this drop. The paper S was sealed with melted beeswax between the two halves of the permeability cell A so no air could leak in at the edges. For most of the tests this cell was made of two glass funnels butted together. Although the effective area of the specimen was not known, it was constant for a given specimen at the different absolute pressures. When measurements were made on the capillaries of the instrument shown in figure 1, these capillaries were connected in place of the permeability cell A of figure 2. The air flow was measured with the calibrated capillary C. Kerosene manometers were used to measure the pressure drop across this capillary and that across the specimen S. The apparatus was tested for leakage at the maximum value of p which was to be used. The volume of air passing through the test piece was, as usual, expressed in terms of the inlet pressure on it. The air flow was first measured at atmospheric pressure with the capillary R disconnected, and then at pressures 2 to 11 percent lower than atmospheric, as shown at the head of each column in table 7.

TABLE 7.—*Increase in air flow with decrease of absolute pressure*

Material tested	Increase in air flow over that at a pressure of one atmosphere at various decreases in absolute pressure									
	2	3	4	5	6	7	8	9	10	11
	Per-cent	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*
Glass capillary 1			0.4		0.2	0.6			0.7	
Glass capillary 2										−0.2
Glass capillary 3				0.4		−.1			−.2	.5
Glass capillary 4			−.3			.0			−.1	
Glass capillary 5		0.2				−.2			.3	
Printing paper			2.0		2.1					2.9
Lined strawboard	0.6		1.2		1.4		1.8		2.9	
Ledger paper	.4	1.1			2.2		2.8			4.0
Bond paper	1.0		1.1	1.3	1.8		2.5			2.7
Coated book paper					3.6			5.3		
Double-coated book paper									7.5	
Alundum disc									.5	

The data in table 7 indicate that the effect of change in absolute pressure on the flow of air through the glass capillaries is negligibly small, being both positive and negative and of about the magnitude of the experimental uncertainty. Number 1 of this group was the only one which appeared to show a consistent, slight increase. It is the one which might be expected to show the least effect, since it has the greatest ratio of length to diameter and, by the criterion of pressure difference, conforms very closely to rates of flow as predicted by the Meyer equation.

All the papers show an appreciable increase in air permeability with decreasing absolute pressure, and this increase approaches that predicted for an orifice-like structure. At first sight these data appear in sharp contrast with the nearly perfect agreement for a capillary-like structure of paper which we have found by all the other criteria applied. Some of the results in table 7, however, are too great to be explained on the assumption that the air passages do not behave as capillary tubes. Even if we should assume the air passages to be outright orifices, the greatest increase in air permeability which equation 6 would predict for the absolute pressure range in table 7 is about 5 percent. We note, however, that the last paper listed shows an increase of 7.5 percent. Moreover, this paper is well formed and of low permeability. When viewed under the microscope there is nothing to suggest air passages comparable in width to the thickness of the sheet. In fact, by the pressure-difference criterion, the air passages behave as long capillary tubes. Some other explanation must be found for the increase in air permeability of the papers in table 7. The most likely explanation is a slight expansion of the structure of the sheet when the pressure on the surfaces is reduced, rather rapidly, in the experiments. The expansion in the structure must be elastic, because the air permeability at a given absolute pressure is nearly always a reproducible quantity. An extremely small expansion would be sufficient to account for the results, since the rate of flow of air through a capillary varies as the fourth power of the diameter. The reproducibility of the data for a given decrease in the absolute pressure suggests that the expansion of the structure may be associated with expansion in those voids which do not communicate with the exterior.

If the hypothesis of expansion of the structure is correct we should expect a structure that is more rigid than paper to show a smaller effect for a given change in absolute pressure. An alundum disk about 2 mm thick and more porous than any paper in table 7 was tested in the apparatus of figure 2, and the result is given as the last entry in table 7. The effect of a 10 percent change in absolute pressure was barely perceptible.

Whether or not the apparent expansion of the structure indicated by these data would occur at higher altitudes is an open question. It may be a variable with differences in barometric pressure, or it may have been brought about by the comparatively rapid exhaustion of the air from the apparatus. From the practical standpoint, however, the influence of absolute pressure cannot be very significant in the testing of paper. In any given locality the fluctuation in barometric pressure is seldom greater than 1 or 2 percent of the mean annual value. Hence the uncertainty in air permeability measurement resulting from changes in absolute pressure would seldom be as much as 1 percent at a given place, even if we accept the data of table 7 as indicative of the effect of differences in barometric pressure. Great differences in altitude would, of course, bring the question into more prominence.

III. NATURE OF THE AIR PASSAGES IN PAPER

With the exception of the absolute pressure data, all the evidence which we have been able to focus on the question has indicated capillary phenomena within the structure of the sheet, and the apparent contradiction in the absolute-pressure data is easily explained on other grounds. The criteria of pressure difference, temperature, and thickness showed a remarkably close correspondence between experimental data (except for thin, poorly formed paper) and the theoretical equations for the flow of air through long, capillary tubes. This excellent agreement between experimental air-flow data and the theory of flow in capillary tubes is a noteworthy circumstance and throws considerable light on the structure of paper. It is certain that the thickness of the paper does not represent the length of the path through the paper, as has frequently been assumed. In order for the rate of flow of air through a capillary to be nearly proportional to the pressure drop, according to the Meyer equation, the length of the capillary must be very great in comparison with the diameter, of the order of a thousand times as great. Of the four glass capillary tubes in the instrument, only the smallest satisfied this criterion. The ratio of its length to its diameter is about 1,300. The corresponding ratio of the next larger, which failed by some 2 or 3 percent of satisfying this criterion within the pressure range studied, was about 750. Although we have little information about the behavior of meandering capillaries of irregular cross section, we cannot escape the conclusion that the length of the air passages through paper as compared with the width of these passages must be very great, in order for the air permeability data for paper to satisfy the theoretical equation for an ideal capillary. Knowing that there is great variation in size and shape of these air passages, and appreciating the tortuous course the air must pursue that the path may attain a sufficient

length, we find it all the more remarkable that the data should agree so well with the theoretical equation for the simple case. The vegetable fibers of which paper is made are, of course, minute capillary tubes of fairly regular cross section. But during the preparation of the fibers the longer ones are cut into sections and considerable breaking down of the walls occurs. In the fabrication of the sheet the fibers become intricately entangled and pressure is applied to the sheet.

In the finished sheet, therefore, a round, straight, tubular passage would be so rare as to be inconsiderable. Some contend that the fiber canals play a minor role in the mechanism of transfer of a fluid through the sheet, the presumption being that the interstitial labyrinth provides chiefly the means of passage of the fluid. It is more probable, however, that both sets of passages are involved, since the wood fibers, which are so short as to require little cutting, contain many small orifices, or pits, through the walls, and the longer fibers, which do not contain the pits, are cut into sections open at both ends. An examination of cross sections of sheets of paper indicates that the fibers are usually much flattened and so closely compacted that the passages both within the fibers and between the fibers are ribbon-like, and that the widths (narrower dimension) of both kinds of passages are of about the same order of magnitude, which one estimates to range for the most part from about 1 to 10 microns. There are, of course, a considerable number of "caverns" of larger size, which presumably communicate with the labyrinthine pattern. In order for the length of the path of air through the sheet to be 1,000 or more times as great as the width of these passages, the path must be at least a few millimeters long (the order of magnitude of the length of the fibers in paper). But the thickness of some of the papers that behave according to the theoretical behavior of a capillary is considerably less than a tenth of a millimeter. The significant fact, which these data bring out, is that the lateral component of the length of the path of air in passing through a sheet of paper must be rather large in comparison with the normal component, which is the thickness of the paper. The tortuous course pursued may perhaps be something like 100 times the thickness of the sheet.

IV. SUGGESTIONS FOR A STANDARD METHOD OF MEASURING THE AIR PERMEABILITY OF PAPER

1. NOMENCLATURE, DEFINITION, AND UNIT OF EXPRESSION

Several terms have been used rather loosely in the literature to describe the permeability of paper to air. In addition to air permeability, terms such as porosity, density, and air resistance have frequently been used almost interchangeably. Although air permeability is related to porosity and density, the test does not measure either. Air resistance, as sometimes used in paper testing, is reciprocally related to air permeability. This term is used in a very different sense in aerodynamics. Of the several designations, air permeability is the preferable term, since the primary definition of permeability relates to the ability of a material to permit the passage of a fluid through its porous structure. This is what is actually measured.

The definition of air permeability is difficult to set down in a single statement, since there are so many factors involved. In view of

what has been learned in this investigation, perhaps the most logical and comprehensive definition is the following:

The air permeability of a fibrous sheet is measured by the limiting value, as the pressure difference approaches zero, of the ratio of the volume of air which passes in unit time through a unit area of the material to the pressure difference, the volume being measured at the pressure on the inlet surface of the material, and the air in contact with this surface being, throughout the test and for a sufficient time prior to the test for the establishment of hygrometric equilibrium, at a temperature of 21 degrees Centigrade, at a relative humidity of 65 percent, and at a pressure of one standard atmosphere. The limiting value of the ratio mentioned above is chosen because, according to equation 5, it is proportional to a structural constant of the sheet.

For all except a few unimportant, thin papers, the ratio in the above definition is numerically equal to the volume of air that flows through the material per unit time, area, and pressure difference. Hence, for nearly all purposes, it is more convenient to define the air permeability of paper and fiber boards in the following manner:

The air permeability is measured by the volume of standard air which passes in unit time through a unit area of the material when urged by a unit pressure difference (not exceeding about 10 g/cm^2) between the surfaces of the sheet. Standard air, for the purposes of this test, is defined as air at 21 C, at 65 percent relative humidity, and at a pressure of one standard atmosphere.

It is unfortunate that we cannot omit the absolute pressure requirement from the definition of air permeability, as the theory of capillary flow would permit within the ordinary range of barometric pressures. It is very inconvenient to require a definite barometric pressure for the air in which air permeability tests are made, but, since the investigation has failed to show the air permeability independent of the absolute pressure, we must for the present include a standard barometric pressure in a precise definition. Fortunately, the fluctuations of barometric pressure in a given locality are small enough that they produce effects within the experimental error of the testing instrument, a circumstance which makes it possible to obtain relative air permeability values without cognizance of the absolute pressure. Since the effect of absolute pressure on air permeability seems to be different for different materials, we have no means of converting air permeability values from one absolute pressure to another. Further investigation of this relation is very desirable in the interest of simplifying air permeability measurements.

Units of expression of air permeability are almost as numerous as are the designs of apparatus for making the measurement. The time required to displace a given volume of air through the test specimen is perhaps the most popular mode of expression. Few investigators have attempted to express the results so as to be intelligible in the absence of specific information about the apparatus and experimental conditions. Metric units, English units, and absolute units have been used. To conform to the definition suggested above, the unit of expression must involve the volume of standard air which flows through a unit area of the material in unit time for a unit pressure difference. The unit which has been found convenient in this investigation expresses the volume in cubic centimeters, the time in seconds, the area of material in square meters, and the pressure difference in

grams per square centimeter and is abbreviated to: $cm^3/sec/m^2/g/cm^2$. Although comprehensive, such an expression is rather awkward. Possibly we can look forward to the adoption at some time of a comprehensive definition of the unit of air permeability to which a simple name can be given in the manner customary in the field of electrical units.[25]

2. APPARATUS AND TESTING CONDITIONS

This investigation has provided an accurate method of measuring the air permeability of paper and fiber boards, and, therefore, a means of appraising other methods of making the measurement. It has not, however, included such an appraisal, without which we cannot say to what extent other apparatus might be suitable. As a result of the investigation we can state the essential characteristics of a reliable apparatus. Such an apparatus should be so designed that conditioned air is caused to flow through the specimen, and the apparatus should measure all the air that comes through the area designated as the test area and no air from any other source. This requirement means an effective prevention of leakage across the clamping surfaces and through the edges of the specimen. An easy means should be provided for testing the apparatus as a whole against leakage. The pressure difference obtainable across the sheet should not exceed about 10 g/cm^2, and should be constant while the test is being made.

For precise work the experimental uncertainty should be as small as possible and the testing conditions should conform to the requirements of the definition in the previous section. For most ordinary testing, however, it is probable that an uncertainty of 2 or 3 percent would be permissible in the calibration of the apparatus, in the constancy of the pressure difference, in the value of the pressure difference, in the readings of the instrument, and in the effective area of the specimen. The absolute-pressure effect will, in general, be within this range of experimental uncertainty for stations under 2,000 feet above sea level. The air passing through the paper should be at 21 C and 65 percent relative humidity, the standard paper testing conditions. The material tested should be in hygrometric equilibrium with this air.

WASHINGTON, March 19, 1934.

[25] The name "perm" has been suggested for the fundamental cgs unit for the permeability to gases of all porous sheet materials. The "perm" would be defined as the volume of gas in cubic centimeters which flows per second through 1 square centimeter of the material under a pressure difference of 1 dyne per square centimeter ($cm^3/sec/cm^2/dyne/cm^2$). Practical units of convenient magnitude would then be derived from this fundamental unit. This would form a logical basis for the correlation of the numerous units of permeability to gases used by different investigators and in different fields. The author wishes to acknowledge his indebtedness to H. D. Hubbard of the staff of the Bureau of Standards for these suggestions.

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A STUDY OF THE PROPERTIES OF MORTARS AND BRICKS AND THEIR RELATION TO BOND

By L. A. Palmer and D. A. Parsons

ABSTRACT

The water retaining capacity, transverse and compressive strengths, sorption, volume changes, and moduli of elasticity of 50 mortars and the absorption rate, moisture expansion, and transverse and compressive strengths of six makes of brick were studied. Also, 15 of the 50 mortars were used with the 6 makes of brick in tests of brick,mortar assemblages. The data indicate that the water retaining capacity of mortars and absorption rate of bricks were of primary importance in obtaining a good bond. The possible effects of brick and mortar properties on strength of bond in tension, bond durability, transverse strength of brick beams, and compressive strength of brick piers are discussed.

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I. INTRODUCTION

1. PURPOSE AND SCOPE

It has been the consensus of opinion among recent writers [1] [2] [3] [4] that the points in brickwork most accessible to the entrance of water are the junctures of brick and mortar. Laboratory data as well as field observations have supported this view.

Suggestions for improving the bond of mortar to bricks or other building units are numerous and conflicting. However, there has been a conspicuous lack of data. This is mainly because it is exceedingly difficult to carry on an investigation so comprehensive and exhaustive that all classes of the materials involved may be well represented in the study.

Unfortunately, the selection of materials from the standpoint of their mutual suitability has received too little attention. Obviously it will not suffice to consider the physical properties of either of the two materials, bricks or mortar, as unrelated to the other. Specifications for either material should be written with regard for the other.

The purpose of this investigation [5] was, therefore, twofold. First, it was intended to make a survey, as wide as possible, of the physical properties of both mortars and bricks. Second, it was then proposed to find how these data are related to the bond with particular reference to water tightness of walls, assuming that improving the bond will improve the watertightness of the masonry.

It happened that a rather extensive survey of bricks from various sections of the United States was being completed [6] at the time this study was begun. This earlier study made it possible to select, with a minimum of preliminary work, representative types of bricks.

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[1] F. O. Anderegg, Water-Tight Masonry, The Architectural Record, vol. 70, no. 3, pp. 202-207, 1931.
[2] L. A. Palmer, Water Penetration through Brick-Mortar Assemblages, Jour. Clay Prod. Inst., vol. 1, pp. 19-31, Sept. 1931.
[3] L. B. Lent, Exterior Wall Construction, General Building Contractor, pp. 35-41, Feb. 1932.
[4] Bulletin of the Boston Society of Architects, no. 3, Dec. 1931.
[5] In order to save space some of the data are presented in the form of graphs showing average values. Tables giving the data in more detail may be obtained upon application to the Bureau of Standards, Washington, D.C.
[6] McBurney, J. W., and Lovewell, C. E., Strength, Water Absorption, and Weather Resistance of Building Bricks Produced in the United States; Proc. Am. Soc. for Testing Mats., vol. 33, part II, p. 636, 1933.

2. DEFINITIONS OF TERMS USED IN THIS PAPER

Bond.—The attachment of brick to brick through the medium of an intervening mortar joint.

Bonding area.—The total area, in square inches, of the flat side of the smaller of two bricks adjacent to an intervening mortar joint.

Brick suction.—The amount of water, in grams, absorbed through the flatside of brick immersed ⅛ inch in water for 1 minute.

Bond durability.—The resistance of bond to arbitrary weathering expressed as length of time required to destroy bond or as the lowering of bond strength.

Bond strength.—The tensils stress, expressed in pounds per square inch of bonding area, required to separate an assemblage of two bricks with intervening mortar joint.

Absorption.—A strictly physical process of a body taking up water and refers to mechanically held water.

Sorption.[7]—Refers to moisture added to a body by any or all of the three processes: Absorption (physical), adsorption (physico-chemical), and hydration (chemical).

Water retaining capacity.—The resistance of a freshly mixed mortar to the loss of water by filtration.[8] [9] In this paper the water-retaining capacity is expressed by the flow on the 10-inch table after suction (2 inches of mercury) for 1 minute, on a standard porous base (see table 2).

3. MATERIALS

(a) SAND

Fairly clean Potomac River mortar sand that had passed a no. 8 sieve was used in all tests. The sieve analysis of this sand was as follows:

Passed sieve no.	Retained on sieve no.	Percent
8	14	7.2
14	28	23.7
28	48	50.4
48	100	15.5
100	----------	3.2
		100.0

(b) CEMENTING MATERIALS

There were used 12 masonry cements, two portland cements, and four limes, products of manufacturers in various parts of the United States. These materials are described in table 2. They were received in steel drums and remained in them tightly covered throughout the period of the investigation except at the times that samples were required.

(c) BRICKS

Six makes of bricks were used and their descriptions are given in table 1.

[7] McBain and Ferguson. Jour. Phys. Chem., vol. 31, no. 4, pp. 562–594, 1927.

[8] L. A Palmer and D. A. Parsons, The Rate of Stiffening of Mortars on a Porous Base, Rock Products, vol. 35, no. 18, pp. 18–24, 1932.

[9] J. C. Pearson, Properties and Problems of Masonry Cements, Proc. Am. Concrete Inst., vol. 28, p. 349, 1932.

TABLE 1

Brick no.	Raw materials	Molding process	Rate of absorption	Flat surfaces
1	Surface clay	Dry-press	Relatively fast	Mechanically smooth.
2	Shale	Stiff-mud, end-cut.	Moderate for shale bricks.	Very rough.
3	do	do	Relatively slow	Moderately rough.
4	Surface clay	Soft-mud, sand struck.	Fast, less than no. 1	Smooth but uneven.
5	Fire clay	Stiff-mud, side-cut.	Extremely slow	Relatively smooth for side-cut bricks, also glassy.
6	Surface clay	do	Fast, less than no. 1 and greater than no. 4.	Very smooth for side-cut bricks.

The rates of absorption of bricks 1 and 5 are generally considered extreme, whereas those of nos. 2, 3, 4, and 6 were intermediate. (See fig. 9, p. 629.)

II. TEST PROCEDURE

1. MORTARS

(a) PROPORTIONING

The method of proportioning the 50 mortars has been presented in a publication (page 18, vol. 35 (18), Rock Products, Sept. 10, 1932), which contains a table descriptive of these mortars. For convenience this table, with the addition of water retaining capacity data from that paper, is given here as table 2.

(b) USE OF THE FLOW TABLE AND SUCTION APPARATUS

The flow table and its use in making mortar studies has already been described at length.[10] [11] The Rogers device, used with the flow table in studying the water-retaining capacities of mortars, is illustrated and described on pages 19 and 20 of the Sept. 10, 1932, issue of Rock Products.

TABLE 2.—*Mortars studied*

Mortar designation	Cementing materials used	Description of cementing materials	Proportions (with sand)		Water retaining capacity (flow after 1 minute on standard porous base)
			By bulk volume [1]	By weight [2]	
					Percent
A I	Portland cement no. 1	Gray, typical portland.	1PC:3S	1PC:3.44S	45
A II	Portland cement no. 2	White	do	1PC:3.49S	47
B I	Masonry cement no. 1 [3]	Modified natural cement.	1MC:3S	1MC:4.62S	74
B II	Masonry cement no. 2	Slag and portland cement.	do	1MC:4.36S	65
B III	Masonry cement no. 3	Hydraulic lime	do	1MC:6.14S	41
B IV	Masonry cement no. 4	Slag and hydrated lime.	do	1MC:4.48S	48
B V	Masonry cement no. 5	Mixture of hydrated lime and portland cement.	do	1MC:6.27S	57
B VI	Masonry cement no. 6 [3]	Modified natural cement.	do	1MC:5.09S	61

[1] Dry rodded volumes of sand and of the dry cementing materials. For the lime putties the volumes are of the putties as used.

[2] The weight proportions are based on the dry weights of sand and of the dry cementing materials. For mortars containing lime putty the weight proportion of the lime is based on the dry weight of the putty after drying for 24 hours at 115 C.

[3] Contained metallic stearates.

[10] See footnote 8.

[11] Volume changes in brick masonry materials, B.S. Jour. Research, vol. 6 (RP 321), p. 1003, 1931.

TABLE 2.—*Mortars studied*—Continued

Mortar designation	Cementing materials used	Description of cementing materials	Proportions (with sand)		Water retaining capacity (flow after 1 minute on standard porous base)
			By bulk volume	By weight	
					Percent
B VII	Masonry cement no. 7 [3]	Modified natural cement.	1MC:3S	1MC:4.57S	86
B VIII	Masonry cement no. 8 [3]	Modified portland cement.	do	1MC:5.24S	42
B X	Masonry cement no. 10 [3]	do	do	1MC:4.20S	70
B XI	Masonry cement no. 11 [3]	Modified natural cement.	do	1MC:5.18S	87
B XII	Masonry cement no. 12	Natural cement	do	1MC:4.85S	54
B XIII	Masonry cement no. 13 [3]	Modified natural cement.	do	1MC:4.76S	96
C I	Lime no. 1	High calcium quicklime.	1L:3S	1 dry hydrate [4] 8.12S.	90
C II	Lime no. 2	Dolomitic hydrated lime.	do	1L:10.52S	68
C III	Lime no. 3	High calcium hydrated lime.	1L:3S	1L:9.21S	71
C IV	Lime no. 4	Dolomitic quicklime	do	1 dry hydrate [4] 7.26S.	96
XRa	Portland cement no. 1 and lime no. 1.		1PC:1L:6S	1PC:0.42 dry hydrate [4]:6.88S.	75
XRb	do		1PC:2L:9S	1PC:0.85 dry hydrate [4]:10.31S.	85
XRc	do		1PC:3L:12S	1PC:1.27 dry hydrate [4]:13.75S.	91
XRd	do		1PC:0.15L:3S	1PC:0.06 dry hydrate [4]:3.44S.	56
XSa	Portland cement no. 1 and lime no. 2.		1PC:1L:6S	1PC:0.33L:6.88S	51
XSb	do		1PC:2L:9S	1PC:0.65L:10.31S	55
XSc	do		1PC:3L:12S	1PC:0.98L:13.75S	60
XSd	do		1PC:0.15L:3S	1PC:0.05L:3.44S	56
XTa	Portland cement no. 1 and lime no. 3.		1PC:1L:6S	1PC:0.37L:6.88S	53
XTb	do		1PC:2L:9S	1PC:0.75L:10.31S	63
XTc	do		1PC:3L:12S	1PC:1.12L:13.75S	69
XTd	do		1PC:0.15L:3S	1PC:0.06L:3.44S	54
XVa	Portland cement no. 1 and lime no. 4.		1PC:1L:6S	1PC:0.47 dry hydrate [4]:6.88S.	84
XVb	do		1PC:2L:9S	1PC:0.95 dry hydrate [4]:10.31S.	93
XVc	do		1PC:3L:12S	1PC:1.42 dry hydrate [4]:13.75S.	94
XVd	do		1PC:0.15L:3S	1PC:0.07 dry hydrate [4]:3.44S.	60
YRa	Portland cement no. 2 and lime no. 1.		1PC:1L:6S	1PC:0.43 dry hydrate [4]:6.97S.	70
YRb	do		1PC:2L:9S	1PC:0.86 dry hydrate [4]:10.46S.	82
YRc	do		1PC:3L:12S	1PC:1.29 dry hydrate [4]:13.95S.	83
YRd	do		1PC:0.15L:3S	1PC:0.06 dry hydrate [4]:3.49S.	57
YSa	Portland cement no. 2 and lime no. 2.		1PC:1L:6S	1PC:0.33L:6.97S	61
YSb	do		1PC:2L:9S	1PC:0.66L:10.46S	63
YSc	do		1PC:3L:12S	1PC:0.99L:13.95S	60
YSd	do		1PC:0.15L:3S	1PC:0.05L:3.49S	52
YTa	Portland cement no. 2 and lime no. 3.		1PC:1L:6S	1PC:0.38L:6.97S	52
YTb	do		1PC:2L:9S	1PC:0.76L:10.46S	54
YTc	do		1PC:3L:12S	1PC:1.14L:13.95S	73
YTd	do		1PC:0.15L:3S	1PC:0.06L:3.49S	58
YVa	Portland cement no. 2 and lime no. 4.		1PC:1L:6S	1PC:0.48 dry hydrate [4]:6.97S.	70
YVb	do		1PC:2L:9S	1PC:0.96 dry hydrate [4]:10.46S.	85
YVc	do		1PC:3L:12S	1PC:1.44 dry hydrate [4]:13.95S.	88
YVd	do		1PC:0.15L:3S	1PC:0.07 dry hydrate [4]:3.49S.	61

[3] Contained metallic stearates.
[4] The amount of dry hydrate per unit weight of freshly slaked lime putty was obtained by drying small samples of the putty for 24 hours in an oven at about 115 C.

A mortar of flow between 75 and 85 percent was considered as being of dry consistency. A mortar of intermediate consistency had a flow between 100 and 110 percent and wet consistency refers to mortar of flow ranging from 125 to 135 percent.

(c) MOLDING OF TEST SPECIMENS

The compression test specimens were 2-inch cubes. The method of filling the metal molds was that given in Tentative Specifications and Tests for Masonry Cements, A.S.T.M., Tentative Standards, part I, vol. 32, 1932, page 695.

The method of molding the 1 by 1 by 10 inch bars in the study of shrinkage during early hardening and of the 1 by 4 by 12 inch specimens in the study of later volume changes, sorption, and moduli of rupture and elasticity has already been described.[12]

(d) CLASSIFICATION OF TEST SPECIMENS

There were 2 series of strength tests made with the 2-inch cubes. The tests with 1 series were made at the end of 3 months, and those of the other series at the end of a year. There were 9 cubes (3 of each consistency, dry, intermediate, and wet) for each mortar in each of the 2 series, a total number of 900 cubes for the 50 mortars, 450 for each test series.

Tests for sorption and volume changes subsequent to hardening were made only with 1 by 4 by 12 inch slab specimens of the series that were kept for a year and tested for transverse strength and modulus of elasticity at the end of that time. Tests for transverse strength and modulus of elasticity at 3 months were made with the other (3 months) series. There were 900 slab specimens, 450 for each series.

For each test for shrinkage during hardening there were three 1 by 1 by 10 inch specimens of each mortar of each consistency, a total of 450 specimens for the 50 mortars.

(e) CURING OF SPECIMENS

All specimens were made and kept for 1 week in a constant-temperature constant-humidity room (relative humidity, 60 ± 5 percent and temperature $70 \pm 2°$ F). All specimens except the 1 by 1 by 10 inch bars were then kept for 3 weeks in a room of high (95 percent or more) relative humidity, the temperature of which was $70 \pm 4°$ F. They were then dried in the laboratory for 2 months. The specimens of the 3-month series were then tested and those of the other series were alternately stored for 1 month in the high-humidity room and for 3 months in the laboratory until they were a year old.

The laboratory temperature ranged from 56 to 94 F, the average being about 68 F. The relative humidity varied from 20 to 85 percent, but usually was within the limits, 30 to 50 percent.

(f) METHODS OF TEST

The equipment used for determining transverse strength and modulus of elasticity and the method of computing data are presented in Bureau of Standards Research Paper 477, pages 384 to 389.

Compression tests were made in accordance with Federal Specification SS–C–181. Par. F–3–g–6.

[12] See footnote 11.

The method of measuring linear changes, both those attending early hardening and those produced subsequent to hardening by alternate wetting and drying, has already been described.[13] Sorption during 15 minutes and 2 hours was obtained by immersing completely in water the slab specimens of the year series at the ages of 3 and 11 months.

2. BRICKS

(a) PREPARATION FOR TESTS

Before being tested, all bricks were dried in an oven (115° to 150° C) to constant weight.

(b) MEASUREMENTS

The method of determining the rate of absorption with 15 representative bricks of each make is described fully under "Method of Procedure" in Bureau of Standards Research Paper 88, p. 118.

The transverse and compressive strengths, obtained with 25 specimens of each make of brick, were determined in accordance with standard A.S.T.M. specifications.[14]

The method of measuring "moisture expansion" produced by prolonged wetting was the same as that used previously.[15]

The rates of absorption of bricks nos. 1, 2, 4, and 6 following total immersion for 15 minutes in water were also determined. The method was the same as that used in the case of dry bricks.

3. BRICK-MORTAR SPECIMENS

(a) PREPARATION OF MATERIALS

Bricks 1, 2, 4, and 6 were set under 2 conditions, namely, dry and after having been totally immersed for 15 minutes in water. Bricks 3 and 5 were set dry in all cases.

Only mortars of intermediate consistency (flow of 100 to 110 percent) were used in making the assemblages.

(b) METHOD OF FORMING TEST SPECIMENS

The mortar joints were approximately ½ inch thick. The procedure followed in bedding the bricks in mortar and in placing ⅜ inch brass lugs when used in the joints has been described.[16]

All test specimens were made in the constant temperature-constant humidity room and, except series 5A remained there for a week after being made.

(c) CLASSIFICATION OF TESTS

A classification of the tests is made on the basis of method of exposure, type of specimen, and purpose of the test. There were six methods of exposure, designated as A, B, C, D, E, and F in table 3.

The test specimens are classified and described in table 4.

(d) MEASUREMENTS

The method of measuring strength of bond is described in detail in a previous publication.[17]

[13] See footnote 11.
[14] Standard Method of Testing Brick (Compression, Flexure, and Absorption) (C 67-31), 1933 Book of A.S.T.M. Standards, pt. II, p. 128.
[15] See footnote 11.
[16] Durability and Strength of Bond Between Mortar and Brick, B.S. Jour. Research, vol. 6 (RP 290), p. 473, 1931.
[17] See footnote 16.

TABLE 3.—*Exposure of brick-mortar test specimens*

Exposure designation	Aging period	Description
	Months	
A	3	First week in constant-temperature constant-humidity room,[1] then 3 weeks in high-humidity (relative humidity 95 percent or more) room, followed by 2 months in the laboratory.
B	12	Exposure during first 3 months, same as A. This was followed by alternate wetting for 1 month in the high-humidity room, and drying for 3 months in the laboratory.
C	12	First week in constant-temperature constant-humidity room,[1] followed by alternate drying for 18 days in the high-temperature low-humidity room,[2] then wetting for 8 days by partial immersion, again drying, wetting, etc., until specimens were 1 year old.
D	[3] 18	First year, same as C. This was followed by 5 cycles of alternate freezing and thawing (see footnote 17), then dried for 18 days in the high-temperature low-humidity room,[2] followed by freezing and thawing (see footnote 17), drying, etc., until specimens had undergone a total of 35 freezings and thawings.
E	3	First week in high-temperature low-humidity room,[2] then 3 weeks in high-humidity room followed by 2 months in laboratory.
F	[3] 7	First 4 weeks same as A. Then 18 days in high-temperature low-humidity room followed by alternate freezing and thawing (5 cycles), drying for 18 days etc. as in D. After 35 freezings and thawings (see footnote 17), specimens were dried in high-temperature low-humidity room [2] for 18 days.

[1] Temperature, 70±2° F., relative humidity, 60±5 percent.
[2] Temperature, 120±5° F., relative humidity, 20 to 30 percent.
[3] Approximate.

TABLE 4.—*Brick-mortar specimens*

Test series designation	Specimens		Materials used	Exposure	Procedure for making specimens	Purpose of tests
	Type	Number				
1A	2 bricks, flat sides bonded.	756. 6 specimens with each mortar and brick set wet or dry.	All bricks, 1 to 6 incl., mortars XVa, XVb, XTd, C II, B VI, B IV, B III, BXI, XRa, XRc, B I, A I, C I, C III, and C IV, 15 mortars representative of the 50 listed in table 2.	A	Bricks 3 and 5 set dry with all 15 mortars. Bricks 1, 2, and 6 set wet [1] with all mortars and dry with all mortars except C I, C III and C IV. Brick 4 set wet [1] with all mortars.	To relate the properties, water retaining capacity of mortar and absorption rate of brick, to strength of bond at 3 months.
2A	do	540. 6 with each brick and mortar.	All of the 15 mortars listed above, all of the 6 makes of bricks.	B	Bricks 1, 2, 4, and 6 set wet [1], nos. 3 and 5 set dry with all of the 15 mortars.	To study the increase in strength of bond with time.
3A	do	270. 3 with each brick and mortar.	do	C	Same as 2A	To determine the effect of volume changes in mortar subsequent to hardening on the strength of bond.
4A	do	72. 12 specimens for each brick immersion period.	Mortar XRa and brick no. 4	F	Bricks set after partial immersion in water for 0, ¼, 1, 3, 5, and 15 minutes.	To relate durability of bond to absorption rate of brick.
5A	do	108. 6 specimens with each brick and each mortar.	Mortars A I, C I, XRc, XVb, B IV, B XI, C II, XRa, and XTd. Bricks 3 and 5.	E	All bricks set dry; half of specimens in each case with, and half without, 3/16-in. brass lugs in joints.	To study the effect of shrinkage during early hardening on the strength of bond at 3 months.
6A	do	216. 6 specimens with each mortar and brick set wet or dry.	Mortars A I, B I, B III, B XI, XRa, and XRc; bricks 1, 4, and 6.	A	Bricks set both wet [1] and dry; 3/16-in. brass lugs embedded in all joints.	To study the combined effect of rapid stiffening of mortar through rapid water loss and shrinkage during early hardening.
7A	do	270. 3 specimens with each brick and mortar.	All bricks, all mortars listed under series 1A.	D	Same as 2A	To observe the effect of possible volume changes subsequent to hardening on the durability of bond.
8A	do	108. 6 specimens with each brick and mortar.	Bricks 2, 3, and 4; mortars A I, B I, B IV, B XI, XRa, and XRc.	F	Brick 3 set dry and bricks 2 and 4 set wet [1] with all mortars.	To determine (by comparison with 7A) the relative degrees of bond durability of specimens subjected to freezing and thawing at different ages.
1B	2 bricks and 2 bats set flatwise with bats between the whole bricks. Vertical joint between bats. All joints ½-inch thick.	24. 6 specimens with each mortar.	Bricks 3 and 6; mortars A I and XTd.	D	Brick 3 set dry with both mortars. Brick 6 set wet [1] with both mortars.	Same as 7A.
1C	Brick piers, 5 bricks, 4 intervening ½-in. joints. Bricks set flatwise, one above another.	270. 3 specimens with each brick and mortar.	All of the 15 mortars listed under 1A above. All bricks.	A	Bricks 3 and 5 set dry and 1, 2, 4, and 6 set wet [1].	To determine the strength of brick beams in flexure at 3 months.
2C	do	do	do	B	Same as 1C	To determine strength of brick beams in flexure at 1 year.

[1] Immersed in water for 15 minutes.

Durability of bond was studied by cyclic wetting, freezing and thawing and drying. Wetting by partial immersion for 48 hours preceded each group of 5 freezing and thawing cycles. The saturated specimens, partially immersed, remained for 18 hours in a freezing chamber after which they were kept under water at room temperature for 6 hours and thus thawed. The freezing temperature varied from about 12° to 30° F., being usually within the limits, 15° to 24° F. The specimens were dried for 18 days in the high-temperature low-humidity room (see footnote, table 3) after each 5 cycles of freezing and thawing. Specimens were subjected to a total of 35 freezing and thawing cycles with 6 intervening drying periods and another following the completion of the 35 cycles. It was considered that the bond had failed, when on lifting the specimen by the top brick, the lower one dropped off.

The equipment for measuring the transverse strength of brick beams (series 1C and 2C, table 4) was the same as that used for determining the transverse strength of brick.[18] The span in this case, however, was 11 inches, approximately the distance from the midpoints of the edges (faces) of the two bricks at opposite ends of the 5-brick 4-joint beams. The total overhang was thus the weight of 1 brick and this was taken as the mean of 25 separate weighings of individual bricks (dry) of each make. The load was applied at the middle of the beam.

The modulus of rupture (lb per sq in.) was computed from the formula:

$$\mathrm{MR}=\frac{3}{bd^2}\{x[P+p(1-x/11)]\}$$

in which: P is the applied load, pounds, p is the weight of the beam, minus the weight of the overhang, b and d are the width and depth (inches), respectively, of the beam at the section of failure, and x denotes the distance of this section from the nearer support.

Usually failure was at one of the two joints adhering to the middle brick, and 3-brick piers (2 intervening joints) were taken from the broken beams for compression tests, performed according to the procedure followed in testing half bricks.[19]

III. RESULTS

1. MORTARS

(a) WATER-RETAINING CAPACITY

As a brief résumé of the results of tests for water-retaining capacities of mortars already published [20] it may be said that the slaked lime putty and stearated masonry cement mortars (made from the natural cements) were found to be the most retentive of water of all of the 50 mortars according to the method of test. The partial substitution of the slaked lime putties for the two portland cements produced a considerable increase in water-retaining capacity above that of the straight portland cement mortars which were among the lowest with respect to this property. The presoaked hydrated limes had much

[18] See footnote 14.
[19] See footnote 14.
[20] See footnote 8.

the same effect as the slaked lime putties but to a much less extent. The water-retaining capacity of hydrated lime mortars was improved by soaking the limes for 24 hours before mixing.

(b) SHRINKAGE DURING EARLY HARDENING

The results are given in table 5. For the portland-cement-lime mixtures the averages are of all of the combinations of the 2 portland cements and 4 limes for each definite proportion by volume. This averaging of all brands for the portland-cement-lime mixtures explains the magnitude of the deviations from the mean as shown by the maximum and minimum values, in comparison with the deviations for the individual brands of lime and portland cement.

TABLE 5.—*Linear shrinkage during early hardening of 1 by 1 by 10 inch mortar specimens*

[Averages are of 24 specimens in the case of lime-portland-cement mixtures and of 3 specimens for all other mortars. Maximum and minimum values for the lime-portland-cement mixtures are averages of 3 specimens]

Mortar composition	Cementing materials	Mortar designation	Linear shrinkage during initial 48 hours at 3 consistencies		
			Dry	Intermediate	Wet
			Percent	*Percent*	*Percent*
1PC:1L:6S	All combinations of 2 portland cements and 4 limes.		avg 0.28 max .35 (YTa) min .23 (XVa)	avg 0.30 max .35 (XTa) min .26 (YVa)	avg 0.33 max .39 (XRa) min .23 (YVa)
1PC:2L:9S	do		avg .40 max .45 (YTb) min .34 (XRb)	avg .48 max .61 (YTb) min .41 (XRb)	avg .51 max .64 (YRb) min .47 (XRb)
1PC:3L:12S	do		avg .48 max .54 (XRc) min .41 (YSc)	avg .62 max .77 (YRc) min .52 (YSc)	avg .67 max .84 (YRc) min .53 (YTc)
1PC:0.15L:3S	do		avg .21 max .25 (XTd) min .14 (XVd)	avg .24 max .30 (XTd) min .18 (XVd)	avg .25 max .32 (XTd) min .20 (XVd)
			Avg percent	*Avg percent*	*Avg percent*
1PC:3S	PC no. 1	A I	.13	.21	.24
Do	PC no. 2	A II	.18	.24	.31
1L:3S	Lime no. 1	C I	.94	1.11	[1] 1.35
Do	Lime no. 2	C II	.57	.66	.72
Do	Lime no. 3	C III	.68	.75	.83
Do	Lime no. 4	C IV	.59	[1].81	[1].94
1MC:3S	MC no. 1	B I	.29	.37	.46
Do	MC no. 2	B II	.29	.31	.36
Do	MC no. 3	B III	.28	.32	.37
Do	MC no. 4	B IV	.21	.24	.29
Do	MC no. 5	B V	.33	.34	.39
1MC:3S	MC no. 6	B VI	.32	.36	.46
Do	MC no. 7	B VII	.24	.32	.42
Do	MC no. 8	B VIII	.35	.36	.48
Do	MC no. 10	B X	.33	.32	.36
Do	MC no. 11	B XI	.25	.28	.36
Do	MC no. 12	B XII	.40	.52	.60
Do	MC no. 13	B XIII	.46	.58	.62

[1] Specimens measured when a week old. Too soft to measure at 48 hours.

The averages of table 5 are highest for the straight lime-sand and 1PC:3L:12S mortars and lowest for the straight portland-cement-sand mortars. The magnitude of linear shrinkage during the initial 48 hours of the 1PC:1L:6S and the 1PC:2L:9S mortars ranged from a low average, 0.28 percent (average, dry consistency, all 1PC:1L:6S

mortars) to a high average of 0.51 percent (average all 1PC:2L:9S mortars of wet consistency). These values fall within the range of the 12 different masonry cement mortars (0.21 percent, MC no. 4, average for dry consistency, to 0.62 percent, MC no. 13, average for wet consistency).

(c) VOLUME CHANGES SUBSEQUENT TO HARDENING

Typical data are presented in figures 1 and 2. Initial strain-gage readings were taken when specimens were a week old. Expansion

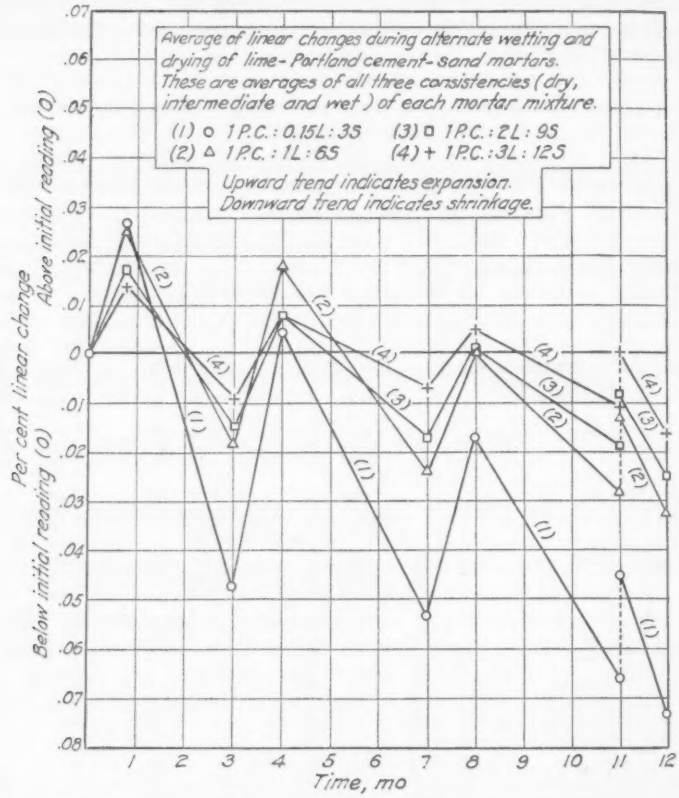

FIGURE 1.—*Typical linear changes in lime-portland-cement mortar specimens subsequent to hardening.*

and shrinkage during subsequent wetting and drying periods were computed with reference to these initial readings. Since only changes in length (not absolute lengths) were measured, the initial points are taken as the origin (specimens 1 week old).

Each plotted point of figure 1 is an average of all three consistencies (dry, intermediate, and wet) and all brands of the materials (lime and portland cement) are included in each proportion by volume as indicated. Each plotted value is, therefore, the average of 72 measurements (3 specimens, 3 consistencies, 8 mortars).

Each plotted point of figure 2 is an average of 9 measurements, 3 specimens with each consistency with each mortar. Masonry cement

mortar B III had the lowest, and B XI the highest volume changes of the 12 masonry cement mortars. The averages of the other 9 masonry cement mortars would, if plotted in figure 2, either coincide with or fall between the plotted values.

The plotted data indicate the extent of variation in linear changes of mortars of different compositions. The highest linear changes were obtained with masonry cement mortar B XI and the lowest with lime mortar C III. Values for the lime mortars were all relatively very low, checking previously published results.[21] Linear changes of the individual 1PC:0.15L:3S mortar mixtures were in all cases slightly higher than corresponding values obtained with the 1PC:3S mortars.

The specimens were subjected relatively more to drying than to wetting, the object being to roughly parallel average climatic conditions. Figures 1 and 2 show relatively more shrinkage than expansion

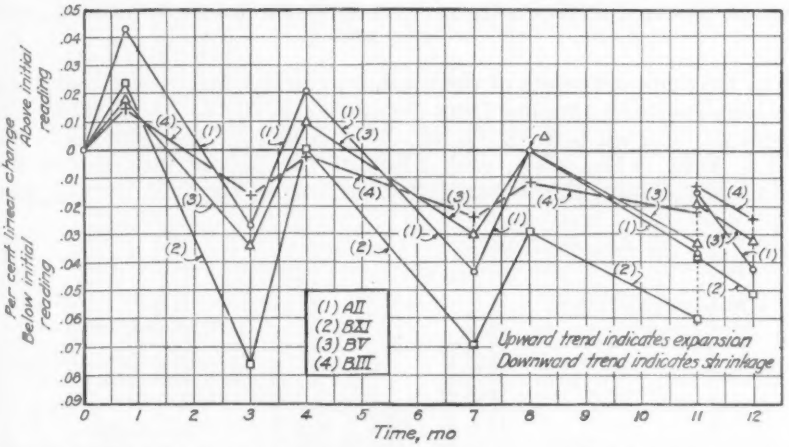

FIGURE 2.—*Typical linear changes in masonry and portland cement mortars subsequent to hardening.*

over the course of a year, possibly due to the preponderance of drying.

It may be noted (figs. 1 and 2) that the greatest shrinkage for all mortars occurred during the first drying period. Of the masonry and straight portland-cement mortars, this shrinkage was greatest for specimens of wet consistency for all mortars except A I, B II, B VI, B IV, and B V, being greatest with dry consistency with mortars A I, B VI, and B II, greatest with intermediate consistency in the case of B V, and there was the same average value with both consistencies, wet and dry, in the case of B IV. The greatest variation with consistency was had with mortar B XII, the average shrinkage being 0.020, 0.034, and 0.041 percent for specimens of dry, intermediate, and wet consistencies, respectively, during the first drying period. The corresponding values in the case of mortar A I in which shrinkage varied least with consistency were 0.061, 0.061, and 0.064 percent, respectively. Thus there was a maximum variation of 100 percent and a minimum of 5 percent between the different consistencies in this group of mortars.

[21] See reference, footnote 11.

In the case of straight lime-sand mortars this variation was relatively high (50 to 300 percent) as would be expected since both the shrinkage and expansion subsequent to hardening in these mortars was relatively very low. The variation in shrinkage with consistency among the portland-cement-lime mortar mixtures was usually less

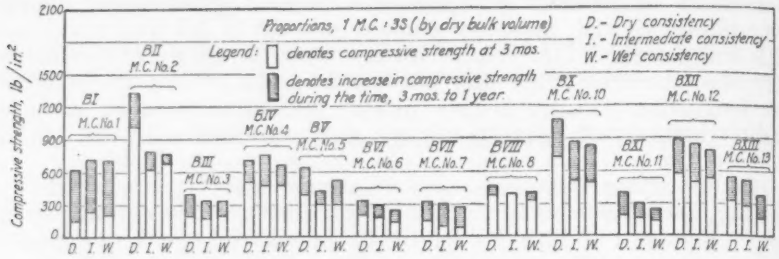

FIGURE 3.—*Average compressive strengths of 2-inch mortar cubes at 3 months and 1 year.*

than that characteristic of the masonry cement and straight portland-cement mortars, ranging from 3 (mortar XTd) to 53 (mortar YRc) percent. For all but 12 (XRd, XSc, XTb, XRc, XVc, XVd, YSa, YTd, YRa, YRc, YVb, and YVd) of the 32 portland-cement-lime mixture mortars, the linear shrinkage during the first drying period

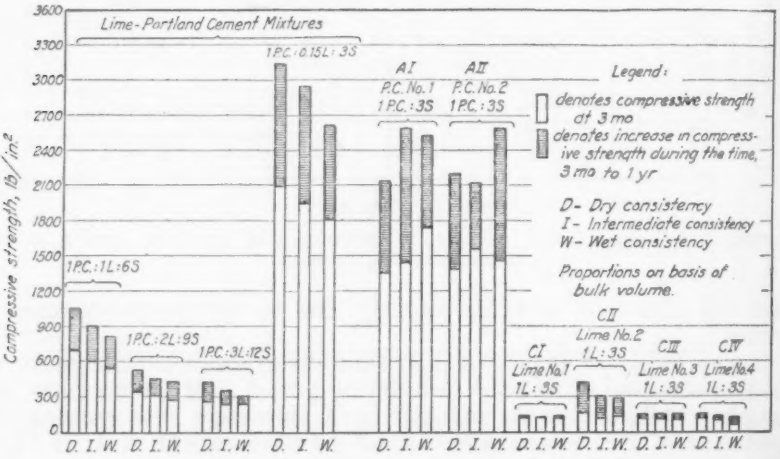
Lime-Portland Cement Mixtures
1 P.C. : 0.15 L : 3S
AI P.C. No.1 1 P.C. : 3S
AII P.C. No.2 1 P.C. : 3S
Legend:
denotes compressive strength at 3 mo
denotes increase in compressive strength during the time, 3 mo. to 1 yr
D- Dry consistency
I- Intermediate consistency
W- Wet consistency
Proportions on basis of bulk volume.
Compressive strength, lb./in.²
1 P.C. : 1 L : 6S
1 P.C. : 2 L : 9S
1 P.C. : 3 L : 12S
CI Lime No.1 1 L : 3S
CII Lime No.2 1 L : 3S
CIII Lime No.3 1 L : 3S
CIV Lime No.4 1 L : 3S

FIGURE 4.—*Average compressive strengths of 2-inch mortar cubes at 3 months and 1 year.*

was greater for wet than for dry consistency. The values for 11 of these 12 exceptions (excluding YRc) indicate relatively small variation with consistency.

In the three specimens of any mortar (exclusive of straight lime-sand mortars) of a given consistency, the maximum deviation from the mean value ranged from 6 to 24 percent, being greatest in the case of those mortars undergoing relatively small changes in length.

(d) COMPRESSIVE AND TRANSVERSE STRENGTH

Compressive and transverse strengths are plotted in figures 3, 4, 5, and 6. In figures 3 and 5 the heights of the vertical columns for the portland-cement-lime mixtures are averages for each consistency of the eight different portland-cement-lime combinations in each of the four definite proportions (1PC:1L:6S, 1PC:2L:9S, 1PC:3L:12S, and 1PC:0.15L:3S) by volume.

It is not apparent from the graphs that transverse strength could always be accurately predicted from compressive strength, or vice

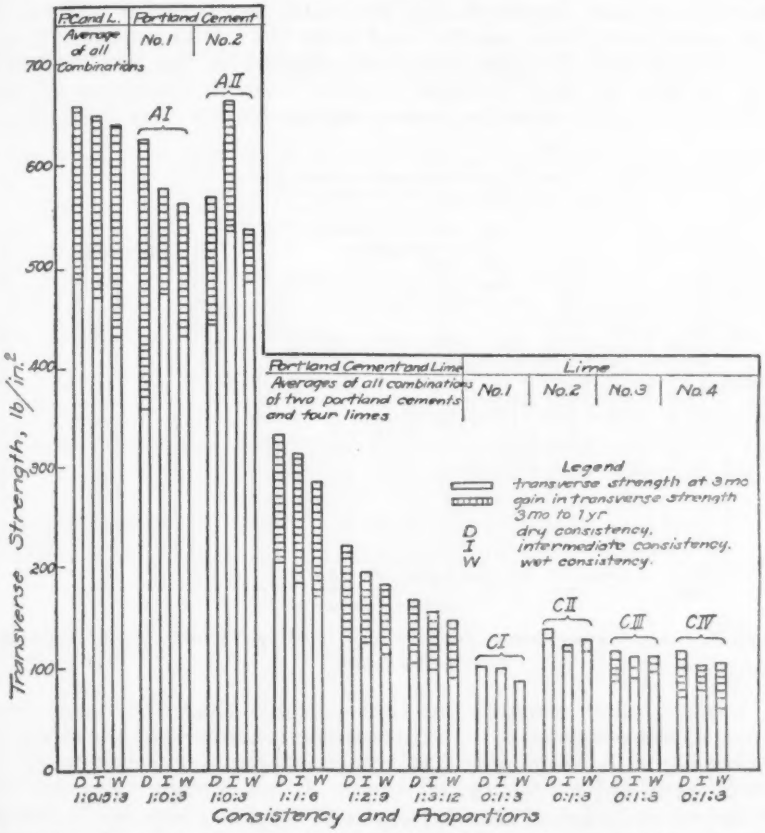

FIGURE 5.—*Average transverse strengths of 1 by 4 by 12 inch mortar slabs at 3 months and 1 year.*

versa. For example, the masonry cement mortars listed in the order of increasing magnitude of transverse strength at the end of a year (considering all consistencies) are as follows: B XI, B VII, B VI, B V, B IV, B VIII, B XIII, B III, B I, B II (B II same strength at 1 year as at 3 months), B XII, and B X. Listing these same mortars similarly on the basis of compressive strength at a year, the order is: B VI, B VII, B XI, B III, B VIII, B XIII, B V, B I, B IV, B XII, B X, and B II (last two nearly equal). The transverse strength test specimens differed materially in size and shape from those used in determining compressive strength.

It is seen, figures 3, 4, 5, and 6, that higher transverse and compressive strengths were associated with drier consistencies, two notable exceptions being portland cement mortars A I and A II which were very low in water retaining capacity. During the first week in the constant temperature room, from visual inspection, specimens of these mortars apparently dried more quickly than specimens of mortars of higher water-retaining capacity. Specimens of mortars of A I and A II of wet consistency retained more moisture during the week's initial drying than those of dry consistency, there being more water initially present in the former case. Hence, it may be concluded that there was a greater degree of early hydration in mortars A I and A II, of wet consistency than was the case when the initial consistency was dry. This may have more than compensated for the fact that ordinarily in wet storage, portland cement mortar specimens of dry consistency would naturally have a higher density (less void space)

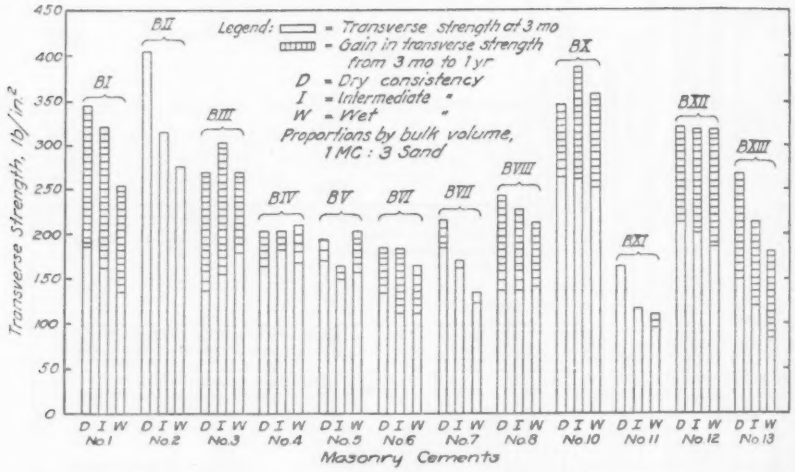

FIGURE 6.—*Average transverse strengths of 1 by 4 by 12 inch mortar slabs at 3 months and 1 year.*

and hence greater strength on that account than specimens from mortars of wet consistency. In this connection note that the strength, compressive and transverse, was highest for dry consistency in portland-cement-lime mortar mixtures. It has already been shown [22] that the substitution of lime for portland cement decreases the water loss by suction. It is probable that water loss through capillary movement and surface evaporation during a few days subsequent to the removal of the cubes from the molds is similarly reduced.

The plotted data of figures 3 to 6, inclusive, show that both the compressive and transverse strength of the mortars which were richer in portland cement than the 1:1:6 mix, were greater than that of the others. The average strength, either compressive or transverse, of the 1 PC:1L:6S mortar mixtures was equal to or greater than that of the strongest of the 12 masonry cement mortars, B II, B X, and B XII, and that of the 1PC:2L:9S mortar mixtures compared favorably with 6 of the masonry cement mortars, B III, B IV, B VII, B VIII, B XI, and B XIII. Moreover, the compressive strengths of

[22] See footnote 8.

both 3 months and year old specimens of the straight lime mortar, C II (lime no. 2), compared favorably with corresponding values obtained with masonry cement mortars B XI, B VII, B VI, and B III. The 1:3 lime mortars, C I, C III, and C IV, were weaker than any of the other mortars.

The strength of a portland-cement-lime mixture mortar was not determined by the strength of either of the two mortars containing only portland cement or only lime, with sand. This is evident from the data of table 6 and figure 3. Possibly the density of the portland-cement-lime mixture, as influenced by its grading, was the most important factor.

TABLE 6.—*Maximum and minimum compressive and transverse strengths of lime-portland, cement mortar mixtures at 3 months and 1 year*

[Values are averages for 3 specimens]

[D denotes dry, I intermediate, and W wet consistency]

Mortar mixture	Compressive strength			
	3 months		1 year	
	Maximum	Minimum	Maximum	Minimum
	Lb/in.²	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*
1PC:1L:6S	888 (XVa-D)	410 (XRa-W)	1,136 (XVa-D)	448 (XRa-W)
1PC:2L:9S	459 (XVb-D)	189 (XRb-W)	750 YSb-W)	302 (XRb-I)
1PC:3L:12S	455 (XVc-D)	134 (XRc-W)	620 (XVc-D)	203 (XRc-W)
1PC:0.15L:3S	2,833 (XVd-D)	1,081 (XRd-I)	3,755 (YSd-D)	1,216 (XRd-W)

Mortar mixture	Transverse strength (modulus of rupture)			
	3 months		1 year	
	Maximum	Minimum	Maximum	Minimum
	Lb/in.²	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*
1PC:1L:6S	282 (XTa-D)	115 (YSa-I)	389 (YVa-D)	178 (XRa-W)
1PC:2L:9S	153 (XTb-D)	80 (XVb-W)	263 (YTb-D)	138 (YVb-W)
1PC:3L:12S	136 (XSc-D)	76 (YSc-W)	209 (XSc-D)	97 (YRc-W)
1PC:0.15L:3S	692 (XTd-D)	187 (XVd-W)	761 (YTd-D)	367 (XVd-W)

Of the portland-cement-lime mortar mixtures, the greatest variation in compressive strength with consistency in any mortar was 82 percent (mortar XVc) and the least was 3 percent (mortar YTc). The density of specimens of mortar XVc varied with consistency to a much greater extent than was the case with mortar YTc. With the portland and masonry cement mortars the corresponding figures are 74 percent (B II) and 11 percent (B XII). In transverse strength measurements, the corresponding variations were 70 percent (XVd) and 5 percent (YTb) in the case of portland-cement-lime mortar mixtures and 63 percent (B II) and 2 percent (B XII) among the portland and masonry cement mortars.

The percentage variations in results obtained with individual mortars of the same consistency were higher generally in the case of compressive strength test data (2 to 41 percent at 3 months and 2 to 28 percent at 1 year) than was the case in tests for transverse strength

(4 to 32 percent at 3 months and 1 to 24 percent at 1 year). Excluding the straight lime-sand mortars, the weakest masonry cement mortars and the 1PC:3L:12S mortar mixtures, the variations among individual specimens of a kind seldom exceeded 10 percent in either transverse or compressive strength tests.

(e) MODULUS OF ELASTICITY AND EXTENSIBILITY

The extensibility of a mortar specimen is the amount per unit of length that the specimen will elongate before rupturing in tension. For the present purpose, extensibility is considered as obtained by dividing the modulus of rupture (MR) by the modulus of elasticity (ME), and the result is expressed as inches per 100,000 inches.

A grouping of the elasticity moduli and extensibilities of all mortars determined both at 3 months and 1 year is given in table 7. The modulus of elasticity varied both with time and consistency as shown in this table. For example, mortar XTd of intermediate consistency when made, had a modulus in the 2,000,000 to 2,250,000 group at 3 months and was in the highest (5,000,000 to 5,500,000) group at 1 year.

TABLE 7.—*Moduli of elasticity and extensibility of mortars at 3 months and 1 year*

[Each number in the second column is the average of 3 tests]

Legend: 3-month-old specimens {d, dry consistency; i, intermediate consistency; w, wet consistency}
1-year-old specimens {D, dry consistency; I, intermediate consistency; W, wet consistency}

Moduli of elasticity group	Mortars in group and their extensibilities × 10^3
Lb./in.²	*Inches per 100,000 inches*
5,000,000 to 5,500,000	XTd: I, 14.
4,500,000 to 5,000,000	XTd: D, 14; W, 15.
4,000,000 to 4,500,000	
3,500,000 to 4,000,000	XSd: I, 18.
3,000,000 to 3,500,000	A I: I, 25. A II: I, 21. XSd: D, 21; W, 22. YTd: D, 24.
2,500,000 to 3,000,000	XSd: i, 24. A I: D, 23. A II: D, 21. YSd: D, 26; I, 25; W, 26. XVd: D, 22. YTd: I, 25; W, 25. YRd: I, 25; W, 28. YVd: D, 28; I, 25; W, 24.
2,250,000 to 2,500,000	XTd: d, 28. YSd: i, 20. YTd: d, 26; w, 24. A I: W, 23. A II: W, 21. XRd: D, 20; W, 20.
2,000,000 to 2,250,000	A II: d, 21; i, 25; w, 26. XSd: d, 27. XTd: i, 31; w, 32. YSd: d, 20. YTd: i, 27. YRd: w, 19. XRd: I, 24. XSa: I, 17. XVd: I, 24. YRd: D, 28.
1,750,000 to 2,000,000	A I: d, 20; i, 26. XSd: w, 27. XVd: d, 25. YRd: d, 20; i, 21. YVd: i, 24. B X: D, 20. XSa: D, 16. XTa: I, 19. B XII: I, 17.
1,500,000 to 1,750,000	A I: w, 28. XRd: d, 29; i, 25; w, 25. XSd: i, 31. XVd: i, 20. YSd: w, 20. YVd: d, 23; w, 22. B X: I, 25. Xsa: W, 18. B II: D, 26. XTa: D, 20. B XII: D, 20. XVa: D, 23. XVd: W, 25. YVa: D, 25.
1,250,000 to 1,500,000	B X: d, 20. XVd: w, 20. B X: W, 24. XTa: W, 18. B XII: W, 21. XVa: W, 21. YSa: D, 25; I, 25; W, 26. YTa: D, 26; I, 26. YRa: D, 25. YVa: I, 23.

TABLE 7.—*Moduli of elasticity and extensibility of mortars at 3 months and 1 year*—Continued

Moduli of elasticity group	Mortars in group and their extensibilities × 10^6
Lb./in.²	*Inches per 100,000 inches*
1,000,000 to 1,250,000	B X: i, 25; w, 20. XSa: d, 23; i, 23. B II: d, 35. XTa: d, 26; i, 22. YTa: d, 20. YRa: d, 21. B III: D, 27; I, 28. XRa: D, 22; I, 19. B VI: D, 16. B I: D, 25; I, 28. XSb: D, 22. B II: I, 28. XSc: D, 20. B XIII: D, 25. B IV: D, 20. B VIII: D, 23. XTb: D, 19. B V: D, 19. XVa: I, 25. XVb: D, 22; I, 21. XVc: D, 19. YSb: D, 25. YTa: W, 28. YTb: D, 23; I, 25. YRa: I, 28. YVa: W, 29.
900,000 to 1,000,000	B III: w, 19. B I: d, 21; w, 14. B II: i, 35; w, 31. B XII: d, 24; i, 25. YTa: w, 19. B III: W, 30. B VII: D, 22. XRa: W, 20. B II: W, 26. B XIII: I, 23. B IV: D, 21; I, 22. B VIII: I, 24. B V: W, 22. XVb: W, 24. Ysb: I, 25. YRa: W, 29.
800,000 to 900,000	B III: d, 17. XSa: w, 25. XTa: w, 28. YTa: i, 20. YRa: i, 23. B VI: I, 20; W, 21. B I: W, 30. XRb: D, 22; W, 23. XSb: I, 20. XSc: I, 22. B XIII: W, 23. B VIII: W, 25. B V: I, 20. XRc: D, 21. YSb: W, 30. YTb: W, 29.
700,000 to 800,000	B III: i, 20. B VII: d, 27. B XI: d, 21. B I: i, 22. XSb: d, 25. B IV: i, 26. B V: d, 24. XVa: d, 26. YRa: w, 23. YVa: d, 21; i, 22. B VII: I, 22; W, 23. B XI: D, 21. XRb: I, 24. XSb: W, 25. XSc: W, 26. XTb: I, 22. XTc: D, 23. XRc: I, 21; W, 18. YSc: I, 26. YTc: I, 25. YTc: D, 24; W, 25. YRb: D, 24. YVb: D, 28.
600,000 to 700,000	B VII: i, 25; w, 21. B VI: d, 22. XRb: w, 24. XSb: i, 22. B XIII: d, 22. B IV: w, 26. B VIII: d, 22; i, 20; w, 21. XTb: d, 23; i, 25. B V: i, 24; w, 24. B XII: w, 28. XVa: i, 25; w, 26. XVb: d, 21. YSa: i, 18; w, 21. YSb: d, 21. YTb: d, 18. YVa: w, 20. XTb: W, 24. XTc: I, 25. YSc: D, 27; W, 26. YRb: I, 26. YVb: I, 25.
500,000 to 600,000	B XI: i, 21. XRa: d, 29; w, 24. B VI: i, 22. XRb: d, 26. XSb: w, 25. XSc: d, 27. B IV: d, 29. XTb: w, 25. XVc: d, 22. YSa: d, 20. YSb: i, 22. YTb: i, 21; w, 21. YVb: d, 21. YVc: d, 21. B XI: I, 23. C II: D, 27; W, 25. C III: D, 21; W, 18. XTc: W, 26. C IV: D, 22; I, 19. YRb: W, 35. YRc: D, 23; I, 20. YVb: W, 28.
450,000 to 500,000	B XI: w, 20. XRa: i, 28. B VI: w, 22. C II: d, 28. XRb: i, 30. B XIII: i, 24. XVb: i, 24. YSb: w, 25. YRb: d, 20. YVb: i, 21. C II: I, 27. C III: I, 24. C IV: W, 21. YVc: D, 22.
400,000 to 450,000	C II: i, 28; w, 26. XSc: i, 29. C III: i, 22; w, 22. XTc: d. 23; i, 24; w, 19. XRc: i, 25. XVc: i, 24. YSc: d, 20. YTc: d, 25; i, 24; w, 24. YRb: i, 24; w, 26. YRc: W, 24. B XI: W, 26. C I: I, 27. YRc: W, 22.
350,000 to 400,000	XSc: w, 28. B XIII: w, 23. C III: d, 24. XRc: d, 25; w, 25. XVb: w, 21. XVc: w, 25. YRc: d, 25; i, 24. YVb: w, 25. YVc: i, 24.
300,000 to 350,000	C I: d, 34; i, 31; w, 27. C IV: i, 25. YSc: i, 26; w, 22. YVc: w, 24. C I: D, 29. YVc: I, 32; W, 34.
250,000 to 300,000	C IV: d, 25. C I: W, 27.
200,000 to 250,000	C IV: w, 26.

The extensibilities of all 50 mortars varied from a minimum of 14 inches per 100,000 inches (XTd intermediate consistency, at 3 months) to a maximum of 35 inches per 100,000 inches (B II, dry consistency, at 3 months). The majority of the values were within the limits,

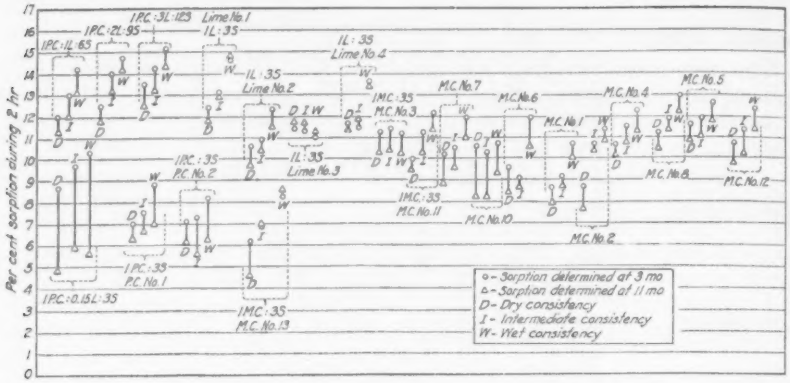
Per cent sorption during 2 hr
o - Sorption determined at 3 mo
Δ - Sorption determined at 11 mo
D - Dry consistency
I - Intermediate consistency
W - Wet consistency

FIGURE 7.—*Average percent sorption of mortar slabs at 3 and 11 months.*

20 to 25 inches per 100,000 inches. There was a slight tendency for the extensibility to increase as the modulus of elasticity decreased and vice versa, but there are many exceptions.

In most cases the moduli of elasticity increased with time. This increase was usually greater than the corresponding increase in

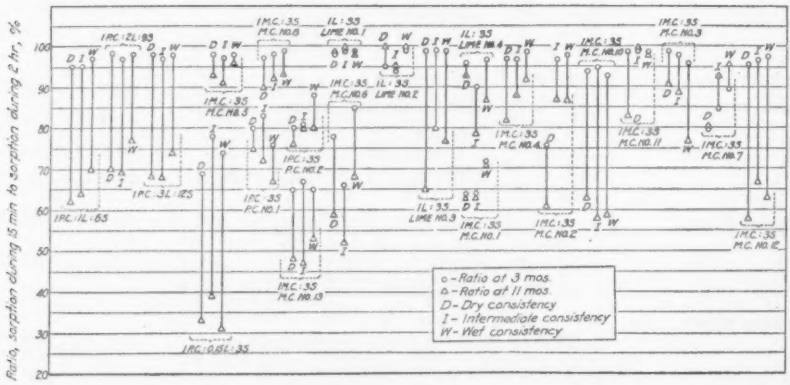
Ratio, sorption during 15 min to sorption during 2 hr, %
o - Ratio at 3 mos.
Δ - Ratio at 11 mos.
D - Dry consistency
I - Intermediate consistency
W - Wet consistency

FIGURE 8.—*Average ratios, sorption during 15 minutes to 2 hours obtained with mortar slabs at 3 and 11 months.*

modulus of rupture, hence the extensibility tended usually to decrease with time.

(f) SORPTION

The sorption data are illustrated in figures 7 and 8. After total immersion for 15 minutes, the specimens were weighed and returned to water where they remained for an additional 1¾ hours when they were again weighed. The ratios, sorption at 15 minutes to that at 2 hours, are plotted in figure 8.

In figure 7 it is seen that in many instances there was an appreciable decrease in sorption (at the end of 2 hours total immersion) at 11 months over that shown at 3 months. Also, the change (increase or decrease) in percent sorption over this period of time was relatively very small in the case of the straight lime-sand mortars. An interesting fact in this connection is that any appreciable decrease in percent sorption during this period was attended by an increase in dry weight (drying in the air of the laboratory). White [23] has made similar observations and discussed them at length.

Each plotted point (figs. 7 and 8) for each of the 4 lime-portland-cement mixtures (1PC:1L:6S, 1PC:2L:9S, 1PC:3L:12S and 1PC:0.15L:3S) is the average of all of the 8 different mortars of the same consistency and of the same mixture. It is important to note that the average sorptions during 2 hours (fig. 7) of the mortar mixtures, 1PC : 1L : 6S, 1PC : 2L : 9S and 1PC:3L:12S, exceeded the average sorptions both of the individual straight lime-sand mortars and the portland-cement-sand mortars. Furthermore, the decrease in sorption over the period, 3 to 11 months, of the 1PC:0.15L:3S mortar mixtures was greater than that of any other mortar. The mortars having lowest sorptions were the 1PC:0.15L:3S, 1MC:3S (MC no. 13), and the two straight 1PC:3S mortars.

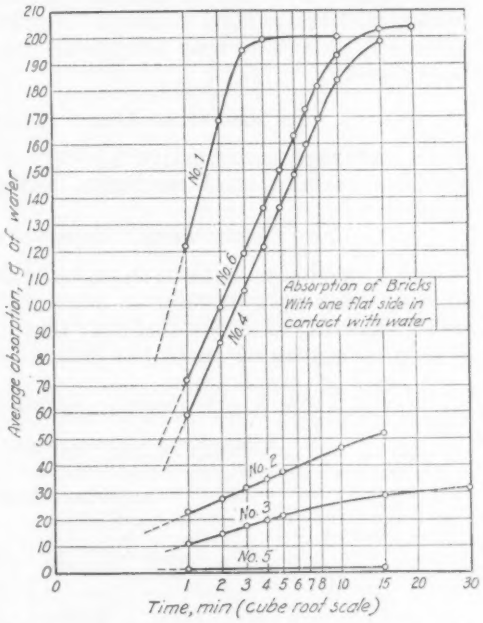

FIGURE 9.—*Average rates of absorption of bricks by partial immersion.*

If the ratio, sorption at 15 minutes to sorption at 2 hours (fig. 8), is nearly unity, then the amount of sorbed water increased relatively slowly with time after the initial 15-minute period of immersion. These ratios decreased with time (3 to 11 months) in practically all cases, the decrease being greatest in the 1PC:0.15L:3S mortar mixture and nearly zero in other cases (lime-sand mortars, limes nos. 1 and 2 and MC no. 1).

The variations in measurements made with the same mortar and the same consistency ranged from 2 to 24 percent, usually not exceeding 12 percent of the mean value.

2. BRICKS

(a) ABSORPTION RATES

Each plotted point of figure 9 is the average number of grams of water per brick absorbed through the flat side areas of 15 specimens of any one make of brick during 1, 2, 3, etc., minute intervals. The

[23] A. H. White, The use of lime in stuccos, Proc. National Lime Association, 1916, p. 109.

average areas of the exposed flat sides of each of the 6 makes of brick were all very nearly equal to 30 sq in (193.5 sq cm). It is seen in figure 9 that with this average amount (grams) of water plotted against the cube root of the corresponding time interval, the points are on straight lines in all cases throughout a certain interval of time, corresponding to the time required for the particular type of brick to wet through from bottom to top, the water rising by capillarity. This linear relationship between the quantity of water absorbed by partial immersion and the cube root of the corresponding time interval, is in agreement with results previously published.[24]

The rate of absorption of brick no. 5 was extremely slow (fig. 9).

The values at 1 minute (fig. 9) were used in subsequent calculations. Total immersion for 15 minutes greatly reduced the absorption by partial immersion for 1 minute. For bricks 1, 2, 4, and 6 these values were 3.2, 2.1, 3.3, and 3.8 grams of water per 30 square inches, respectively.

(b) COMPRESSIVE AND TRANSVERSE STRENGTH

The average compressive and transverse strengths and the individual maximum and minimum values of the 6 bricks are given in table 8.

(c) EXPANSION OF BRICKS ON WETTING

The 5 specimens with each make of brick (3 bricks each, joined end to end) [25] tended generally to expand slowly during prolonged immersion (1 month) in water, but only to a slight extent in any case. This is in good agreement with the data of others.[26]

TABLE 8.—*Compressive and transverse strengths of bricks*

[Each average value was obtained with 25 specimens]

Brick no.	Compressive strength			Modulus of rupture		
	Average	Individual maximum	Individual minimum	Average	Individual maximum	Individual minimum
	Lb/in.²	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*
1	7,435	8,790	6,000	764	880	575
2	6,705	8,480	4,450	2,090	2,870	1,090
3	14,750	18,670	11,150	1,800	3,310	1,210
4	4,330	6,080	3,000	529	740	305
5	16,025	21,170	13,220	2,665	3,340	1,670
6	4,830	7,230	3,650	609	886	424

The linear expansions of the brick specimens during one month in water were 4, 3, 3, 4, 0, and 4 thousandths of a percent for bricks nos. 1 to 6, respectively.

3. ASSEMBLAGES

(a) STRENGTH OF BOND

(1) General Considerations. All of the data obtained with test series 1A to 6A (table 4), inclusive, are plotted in figures 10 and 11. The length of the vertical line connecting all of the points for any one

[24] L. A. Palmer, Some absorption properties of clay bricks, B.S. Jour. Research, vol. 3 (RP88), p. 105, 1929.
[25] See reference, footnote 11.
[26] R. E. Stradling, Department of Scientific and Industrial Research, Building Research Bulletin No. 3, Effect of moisture changes on building materials.

mortar, is an indication of the variability in strength of bond obtained under different conditions. The mortars with which strength of

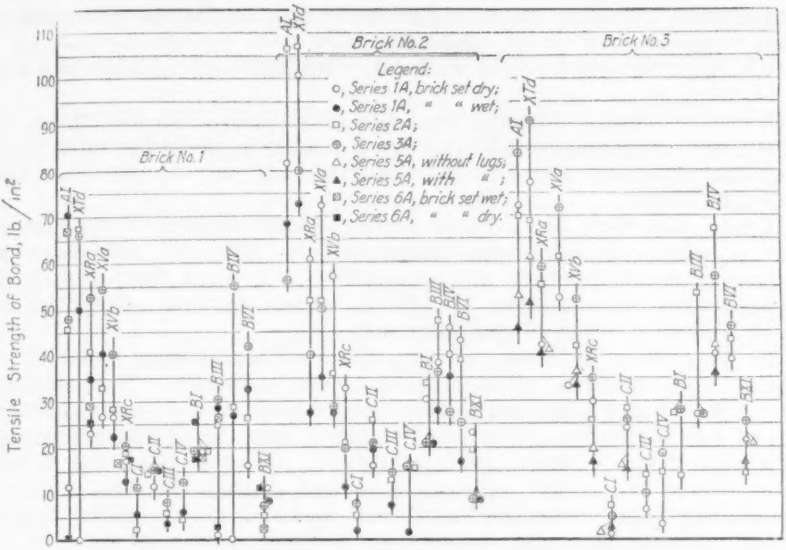
Brick No.1
Brick No.2
Brick No.3
Legend:
○, Series 1A, brick set dry;
●, Series 1A, " " wet;
□, Series 2A;
⊕, Series 3A;
△, Series 5A, without lugs;
▲, Series 5A, with " ;
⊡, Series 6A, brick set wet;
■, Series 6A, " " dry.
Tensile Strength of Bond, lb./in.²

FIGURE 10.—*Average bond strengths in tension obtained with two brick-mortar specimens.*

bond varied least with the conditions were those which had the least variation in extent of bond [27] with the types of bricks included in this

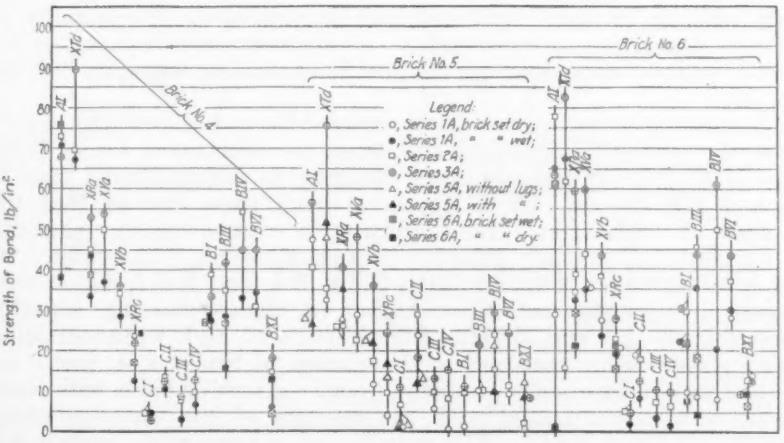
Brick No.4
Brick No.5
Brick No.6
Legend:
○, Series 1A, brick set dry;
●, Series 1A, " " wet;
□, Series 2A;
⊕, Series 3A;
△, Series 5A, without lugs;
▲, Series 5A, with " ;
■, Series 6A, brick set wet;
■, Series 6A, " " dry.
Strength of Bond, lb./in.²

FIGURE 11.—*Average bond strengths in tension obtained with two brick-mortar specimens.*

study. The important consideration is the minimum value obtained with any one mortar and type of brick. For example, the minimum value is zero, with brick no. 1 and mortar XTd (fig. 10) and this was

[27] The fraction or percent of the total flatside area of a brick to which mortar adehres. Extent of bond may be considered as the bonded area and in this investigation it was estimated from visual inspection of broken specimens.

not due to total lack of strength in this mortar but to poor [28] extent of bond, and the minimum values (figs. 10 and 11) are indicative of the poorest extent of bond when the relatively strong mortars are considered. It is evident from figures 10 and 11 that the strength of bond varied over a wider range generally with certain mortars (A I and XTd, for example) than with other mortars (XVb, XRc, B I and B VI, etc.).

It is also equally evident that the maximum bond strengths obtained with all mortars and brick no. 2 tended to be higher than bond strengths obtained with the same mortars and any of the other five makes of bricks.

It may, therefore, be said that a type of building unit may be found that is relatively adaptable under widely different conditions to various types of mortars, and conversely, a type of mortar may be selected that is relatively adaptable under varying conditions to widely different types of building units.

(2) The effect of brick suction, the water retaining capacity of mortar and strength of mortar on bond strength. The average amounts of water absorbed during the first minute of partial immersion of five of the makes of bricks ranged from 10 to 120 grams per 30 square inches of brick surface (fig. 9). That of brick no. 5 was 1.5 g. The "suction" (amount absorbed during the first minute) was slightly more than 20 g in the case of brick no. 2. From figures 12 and 13 note that at 3 months, for a brick suction of 20 g, in all cases, the bond strength is very near the maximum value.

The data, plotted in figures 12 and 13, give curves typical of the other mortars. All of the six makes of bricks set dry and nos. 1, 2, 4, and 6 set wet are represented in figures 12 and 13. The bricks when set wet (after 15 minutes total immersion) were extremely low in suction. It is seen that the bond strength increased from very low brick suction to the maximum and then decreased, gradually or sharply, depending on the mortar. This steepness of descent of the mortar curves depended on the water-retaining capacity of the mortars.

The descent of the curves for mortars XRc and B I of high water-retaining capacity is gradual and those for mortars A I and B III (figures 12 and 13) descend more abruptly as the maximum point is reached and passed. It is apparent from these curves that the mortars of highest strength and lowest water-retaining capacity (A I and B III) actually gave lower bond strength with bricks 1, 4, and 6 set dry than mortars XRc, XRa, B I, and B XI, which were weaker in strength but much higher in water-retaining capacity than mortars A I and B III. The mortars of high water-retaining capacity were more resistant to the suction of bricks 1, 4, and 6 set dry and as a consequence produced greater extent of bond with these bricks than was obtained with the mortars of low water-retaining capacity, A I and B III. The poor extent of bond with mortars A I and B III with the porous bricks accounts for their lower bond strength.

From the standpoint of bond strength, brick no. 2 having a rate of absorption less than that of no. 4 (intermediate, see fig. 9) was better

[28] If the extent of bond was less than 90 percent, it was called poor. Good (practically complete) extent of bond was from 95 to 100 percent. With but very few exceptions the bond was either good or considerably less than 90 percent.

suited to all of the types of mortars studied than any of the other bricks.

The initial steep ascents of all of the curves (figs. 12 and 13) is of interest. Despite the shapes of these curves, there is apparently no

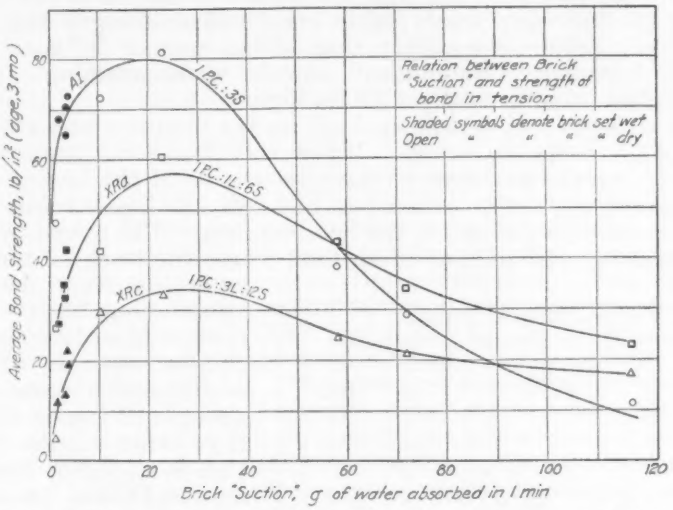

FIGURE 12.—*Bond strength as related to brick suction and water-retaining capacity of mortars.*

justification for extrapolation to zero; it is known that mortars adhere to glass bricks of zero absorption. The bond strengths between zero and about 30 g suction were highest with mortars of high strength. It is evident also from figure 14, in which the maximum bond strengths

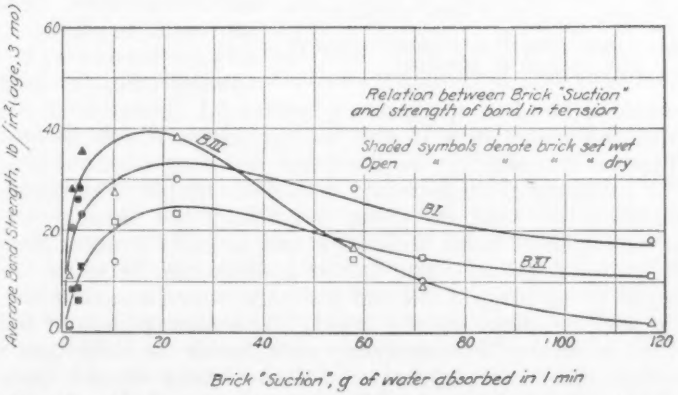

FIGURE 13.—*Bond strength as related to brick suction and water-retaining capacity of mortars.*

of mortars at 3 months are plotted against the logarithm (base 10) of the compressive strengths of the mortars at 3 months, that the bond strengths were highest with mortars of high strength, provided that the extent of bond was good.

When the brick suction was 60 g per minute or greater, the highest strength of bond at 3 months was obtained with mortars of medium

strength and medium or high water-retaining capacity. This is apparent from inspection of the curves in figures 12 and 3. For example, the curve for mortar A I crosses below the curves for XRa and XRc as the brick suction increased beyond 60 g. Moreover, the curves for mortars XRa and XRc approach one another in this region. Mortar A I had very much higher compressive strength and much lower water-retaining capacity than either mortar XRa or XRc. Mortars XRa and XRc differed more in water-retaining capacity (XRc higher) than in strength (XRa higher).

Bond strength was dependent both on the intensity and extent of adhesion of mortar to bricks. When very low bond strength was obtained with the strongest mortars, inspection of the broken specimens showed the extent of bond to be small, the bonded area being often less than 25 percent of the bonding area. The extent of bond was practically 100 percent in all tests where the brick suction was at or less than the optimum (about 20 g). With the extent of bond as good as this, strength of bond was dependent more on the strength of mortar than on any other single factor. This is apparent from figures 10,11, and 14.

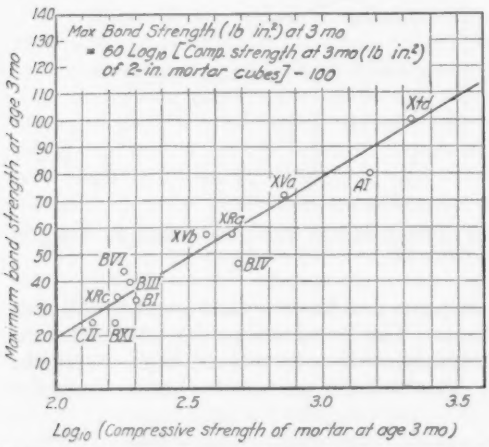

FIGURE 14.—*Bond strength as related to compressive strength of mortars*

(3) The effect of shrinkage on bond strength during early hardening of mortars. Consider mortars A I, XTd, XRa, XVb, XRc, C I, C II, B IV, and B XI, as used with brick no. 3 (set dry), figure 10, and with brick no. 5 (set dry), figure 11. The shaded triangle designates the strength of bond in specimens of series 5A (tested at 3 months) that contained metal lugs in the mortar joints which theoretically would increase any damage to the bond resulting from early shrinkage. The positions of these points should be compared to those of the open triangles (no lugs, all other conditions the same). In some cases the strength of bond with lugs was actually greater than that obtained without them. The vertical distances between the two triangles are in all cases small and indicate, therefore, that the early shrinkage had no effect on the bond. The absorptions of bricks 3 and 5 were low, that of 5 being nearly zero, hence the shrinkage during early hardening of mortars between these bricks should have been comparable to that measured with the specimens of the same mortars cast in metal molds.

(4) The combined effect of shrinkage during early hardening, and of compacting of mortar on a porous base, on bond strength. The previous section dealt with mortars on a practically nonporous base. Freshly-made mortar begins at once to lose water when placed on a porous base, prior to any appreciable hardening of the mortar and with consequent diminution in volume and this compacting on a por-

ous base must be distinguished from shrinkage during early hardening which occurs later. Compacting is minimized when the base is a brick of the types no. 3 or no. 5. However, shrinkage during early hardening would tend to be greater on a nonporous than on a porous base, since reducing the amount of water in mortars tends to reduce this type of volume change (see table 5). Compacting on a porous base is also for the most part unidirectional, i.e., mortar in horizontal joints is compacted chiefly in the vertical direction. Shrinkage attending hardening or cementing action is essentially omnidirectional.

In test series 6A (table 4 and figs. 10 and 11) bricks 1, 4, and 6 were set both wet and dry with mortars A I and B III of low, B I and XRa of medium, and XRc and B XI of high water-retaining capacities, respectively. In this series metal lugs were embedded in all mortar joints. Since compacting of mortar on a porous base is a consequence of water loss to the base, it would be expected that mortars of highest water-retaining capacities would compact least. At the same time such mortars in this case (XRc and B XI) are characterized by relatively high shrinkage during early hardening. The reverse was true for mortars A I and B III. Porous bases were obtained with bricks 1, 4, and 6 set dry. The strength of bond at 3 months with this condition (shaded squares, figs. 10 and 11) should be compared with that obtained when the same bricks were set wet (square with cross, same figures). In the first case the conditions were theoretically conducive to a maximum degree of compacting and a minimum degree of shrinkage during early hardening. The reverse was the case with the bricks set wet.

For mortar A I, brick 1 set dry and with lugs (shaded square, figure 10), the strength of bond at 3 months was very low and less than the strength obtained without lugs and all other conditions the same (series 1A, open circle). The bond strength with no. 1 brick set wet, series 6A (square with cross), was only slightly less than that obtained without lugs, all other conditions being the same (series 1A, shaded circle). In this case, the fact that brick no. 1 was wet or dry when set was of more importance than whether or not lugs were in the mortar joints.

From figures 10 and 11 similar comparisons may be made with each of the mortars A I, B III, B I, XRa, B XI, and XRc and bricks 1, 4, and 6 set both wet and dry, with and without lugs. When these comparisons are made, the following will be evident: no damaging effect on bond strength produced either by compacting on a porous base or by shrinkage during early hardening or by both occurrences was noticeable when metal lugs, designed to increase such an effect by restraining movement (in the vertical direction) of the bricks, were embedded in the joints. A much lower strength of bond was obtained with mortars A I and B III (low water-retaining capacity) with the dry than with the wet bricks whether lugs were or were not present. On the other hand with mortars XRc and B XI (high water retaining capacity), higher bond strengths at 3 months were usually obtained with bricks 1, 4, and 6 set dry with lugs than when these bricks were set wet either with or without lugs. In the case of mortar XRa (medium water-retaining capacity) the bond strength was highest with bricks 1 and 6 set wet and brick 4 set dry. Bricks 1 and 6 each had a higher absorption rate than brick 4.

It is indicated by the process of elimination, that the rapid stiffening of mortars of low water-retaining capacity on a porous base, an occurrence always very noticeable with this combination of brick and mortar types, is the main cause of a poor initial bond. The compacting of the mortar in this case is relatively, at least, of far less importance in its effect on bond strength than rapid stiffening, which renders unlikely a desirable intimacy of contact between the mortar and the unit. It is further indicated that with such desirable contact, there is no significant change in the early bond strength produced by even a relatively high degree of shrinkage during early hardening (characteristic of mortars XRc and B XI).

(5) The effect on bond strength of volume changes in mortar subsequent to hardening. The brick-mortar specimens of series 2A were subjected to only 3 cycles of alternate wetting for 1 month in the high-humidity room and drying for 3 months in the laboratory (curing B, table 3). Those of series 3A were subjected to cycles of drying for 18 days in the high-temperature low-humidity room and then wetting by partial immersion (curing C, table 3). Aside from differences in the number of cycles, the degree of wetting and drying and the temperatures during these exposures all conditions were the same in these two test series. The values in table 9, prepared from the data of figures 10 and 11, show that, of the 15 mortars and 6 brick combinations (total of 90), the bond strengths at 1 year were higher 57 times for series 3A and 31 times for series 2A.

It is seen from table 9 that with all bricks except no. 2, the bond strength at 1 year was usually higher in series 3A. The reverse was true with brick no. 2. Therefore, the strengths were not damaged by the amount of volume change of the mortars subsequent to hardening.

TABLE 9.—*A comparison of bond strengths obtained with test series* 2A *and* 3A

[Six tests were made with each brick and mortar combination]

Mortar	Volume changes subsequent to hardening	Test series with which highest bond strength was obtained					
		Brick no.					
		1	2	3	4	5	6
AI	High	3A	2A	3A	2A	3A	2A
XTd	do	2A	2A	3A	3A	3A	3A
XRa	do	3A	2A	3A	3A	3A	3A
XVa	do	3A	2A	3A	3A	3A	3A
XVb	Intermediate	3A	2A	3A	3A	3A	3A
XRc	do	3A	2A	3A	2A	3A	3A
CI	Low	3A	3A	2A	2A	3A	2A
CII	do	3A	2A	2A	2A	2A	2A
CIII	do	3A	3A	2A	3A	3A	3A
CIV	do	3A	tie	3A	3A	3A	3A
BI	Intermediate	tie	2A	3A	2A	3A	3A
BIII	Low	3A	2A	2A	3A	3A	2A
BIV	Intermediate	3A	2A	2A	2A	3A	3A
BVI	do	3A	2A	3A	3A	3A	3A
BXI	High	3A	2A	3A	3A	3A	2A

It must not be concluded though that with different sands and cements or with mortars richer in cements than those herein described, there could be no damage to the bond through volume changes in the hardened mortars.[29]

[29] See reference, footnote 2.

Inspection of the broken specimens, series 3A and 2A, showed good extent of bond in all cases. Unbonded areas were altogether lacking, a condition not always realized in walls of buildings. There were more surface cracks on mortar joints with mortars A I, XTd, XRa, XVa, and B IV, series 3A, than were noted with these mortars in series 2A. Such cracks, however, which developed during drying, tended to heal during wetting.

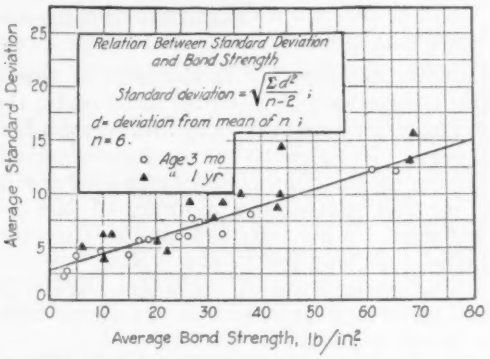

FIGURE 15.—*Average standard deviations computed from test series 1A and 2A as related to average bond strength obtained with 15 mortars and 6 makes of bricks.*

(6) The increase in strength of bond with time. That bond strength increased with time is evident from figures 10 and 11 when a part of series 1A is compared with all of series 2A. All specimens of series 1A were tested at 3 months and those of 2A at 1 year. Note first the relative positions of the shaded circles and the open squares with bricks 1, 2, 4, and 6 (set wet), then those of the open circles and open squares with bricks 3 and 5 (set dry). The vertical distances between the points as indicated varied with the mortar, being generally proportional to the corresponding increase in compressive strength of mortar cubes from 3 months to 1 year (figs. 3 and 4). In a very few instances (mortars B VI and B I with brick no. 1) the bond strength at 3 months was appreciably greater than at 1 year.

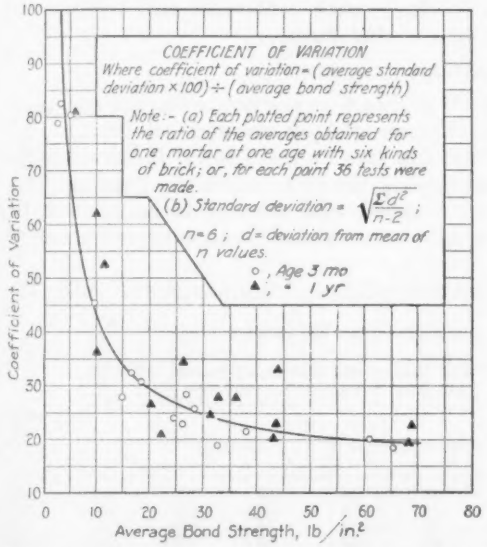

FIGURE 16.—*Coefficients of variation computed from the data plotted in figure 15*

(7) Statistical treatment of bond strength data. Figures 15 and 16 show a relation between bond strength and standard deviation. In obtaining these relations only those specimens in which the extent of bond (noticed on inspection of the broken specimens) was good and for which all conditions including exposure and method of making the specimens were the same have been considered. The results included in the computations, therefore, were those obtained with bricks 1, 2, 4, and 6 set wet with all mortars and bricks 3 and 5 (relatively impervious) set dry with all mortars. This included a part of series 1A (3-month tests) and all of series 2A (1-year tests).

A value was obtained for the standard deviation for each mortar and brick combination and for each of the two test ages (3 months and a year) with the formula:[30]

$$\text{Standard deviation} = \sqrt{\frac{\Sigma d^2}{n-2}}$$

In this formula, Σd^2 is the sum of the squares of the 6 deviations from the mean of n (equal to 6) tests, the number of tests made with 1 brick and mortar combination and at a definite age, 3 months or a year. In figure 15 the average of 6 standard deviations as computed above, all for the same mortar and age but with all 6 makes of brick, is plotted against the average of the 6 corresponding bond strength averages. Each plotted point, therefore, represents the results of tests of 36 test specimens (1 age, 1 mortar, 6 makes of brick).

The coefficients of variation, figure 16 (representing coefficient of variation as related to average bond strength) are the ratios, $\frac{\text{average standard deviation,}}{\text{average bond strength}}$ multiplied by 100.

It is seen in figure 16 that the coefficient of variation increases most rapidly with decreasing bond strength for average bond strengths less than 20 lb/in.^{2} For strength above this value, the change in coefficient of variation is less marked. By selecting materials and conditions such that a bond strength of 20 pounds or more per square inch may reasonably be expected, fairly reproducible and representative bond strength values could be obtained with a fewer number of specimens than would be required when working with materials and conditions likely to yield bond strengths below this value.

(b) DURABILITY OF BOND

Test series 4A, 7A, 8A, and 1B (table 4) were made for the purpose of studying bond durability. Of series 7A, including all bricks and all of the 15 mortars, there were only two cases of bond failure during a year of alternate wetting and drying that preceded the freezing and thawing tests. These failures occurred with mortar B XI used with brick no. 1 and C I with brick no. 6, set wet. Both mortars were of low strength.

The results obtained with test series 7A are summarized in table 10.

TABLE 10.—*Bond durability of 2 brick-mortar specimens (series 7A).*

Mortar	Total number of freezing and thawing cycles endured without bond failure by 3 specimens						Average
	Brick number						
	1	2	3	4	5	6	
A I	105	105	105	105	105	105	105
XTd	105	105	105	105	105	105	105
XRa	58	70	105	54	105	83	79
XVa	65	83	105	105	105	84	91
XVb	15	27	105	10	105	21	47
XRc	14	23	76	11	47	17	31
C I	30	26	13	2	2	0	12
C II	50	85	48	6	9	7	34
C III	14	32	20	7	9	7	15
C IV	6	28	12	0	9	7	10
B I	88	73	105	105	36	105	85
B III	105	105	105	105	105	105	105
B IV	105	105	105	105	105	105	105
B VI	105	105	105	105	105	105	105
B XI	0	57	105	105	35	6	51
Average	58	69	81	62	66	57	65

[30] Biometrika, vol. 10, p. 525.

The number of cycles of freezing and thawing endured without failure given in table 10 is computed by adding the total number of cycles endured by the three like specimens. If one specimen should survive only 13 and the other two 35 cycles, the total number of cycles endured would be 83 as in the case of mortar XVa and brick no. 2. The number, 105, is, therefore, a perfect record and a diminution in total number of cycles endured shows a lessened bond durability under the conditions of test.

Bond durability decreased as more and more lime was substituted for portland cement, the record of XRC, a 1PC:3L:12S mortar being about the same as that of C II, a straight lime-sand mortar. On the basis of approximate strength equality, mortars XRa, XVa and XVb should have been as resistant to freezing and thawing as masonry cement mortars B III, B IV, and B VI which was not the case. There is also another factor to be considered. It is observed (fig. 7) that the sorption of these portland-cement-lime mortar mixtures exceeded that of mortars of masonry cements nos. 3, 4, and 6. The data indicate, therefore, that the two properties, strength and sorption of mortars, were of primary importance in getting bond durability.

Excepting brick no. 3, the average number of bond failures did not vary appreciable with the make of brick. Brick no. 5 set dry had a lower absorption rate than bricks 1, 2, 4, and 6 set wet. Brick 3, also set dry, had an absorption rate somewhat greater than that of the bricks set wet. As indicated in figures 12 and 13, a certain degree of absorption is, within limits, a factor that improves the strength of bond, possibly by increasing the mortar strength (by increasing the cement-water ratio), yet without removing too much of the water from the mortar. This condition was more closely approached by brick 3 set dry in series 7A than by any of the other bricks of that series. This again indicates that an increase in strength of mortar is attended by an increase in bond durability, all other conditions being the same.

The fact that the averages in table 10 of bricks 1 and 6 were lower than those of bricks 2, 4, and 5 may possibly be explained by the fact that the bonding areas of bricks 2, 4, and 5 were more rough and uneven than those of bricks 1 and 6.

The percentage failures of specimens of test series 8A (mortars A I, B I, B IV, B XI, XRa, and XRc with bricks 2, 3, and 4) which were a month old when first subjected to freezing and thawing is compared in table 11 with the corresponding percentage failures of specimens of the same mortar and brick combinations (included in test series 7A) that had aged a year when freezing and thawing was begun.

TABLE 11.—*Percentage of specimen failures*

Mortar	Percentage failures during 35 cycles of freezing and thawing					
	Brick no. 2, aged		Brick no. 3, aged		Brick no. 4, aged	
	1 month	1 year	1 month	1 year	1 month	1 year
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
A I	0	0	0	0	0	0
B I	17	33	17	0	0	0
B IV	0	0	0	0	0	0
B XI	33	67	33	0	50	0
XRa	0	33	17	0	0	33
XRc	[1] 100	[2] 100	[1] 100	33	83	[2] 100
Average	25	39	28	6	22	28

[1] No failures during first 10 cycles of freezing and thawing.
[2] At least 1 specimen survived first 10 cycles of freezing and thawing.

The results (table 11) do not indicate an increase in resistance to freezing and thawing with aging specimens except in the case of brick no. 3.

The results obtained with test series 4A are presented in table 12. In this instance brick suction was controlled by partially immersing 5 groups each of 24 bricks for 0, 1/4, 1, 3, 5, and 15 minutes, respectively. The average suction (g of water per minute per 30 sq in.) was 58 g for bricks set dry and 40, 26, 16, 12, and 3.3 g after partial immersion for 1/4, 1, 3, 5, and 15 minutes, respectively.

TABLE 12.—*The strength of bond of specimens of test series* 4A

[Each average value was obtained with 12 specimens]

Mortar XRa and brick no. 4

Group	Brick suction	Average bond strength	Individual maximum	Individual minimum	Total area of section of failure represented by failure of brick
	g	*Lb/in.*[1]	*Lb/in.*[1]	*Lb/in.*[1]	*Avg percentage*
No. 1	58	49.2	75.5	30.8	25
No. 2	40	48.6	69.4	32.4	19
No. 3	26	50.9	68.3	23.1	35
No. 4	16	50.8	78.4	22.2	40
No. 5	12	55.9	81.5	37.8	10
No. 6	3.3	45.2	67.1	[1].0	0

[1] Failed during freezing and thawing.

After 35 freezing and thawing cycles (with intermittent drying after each 5 cycles) the specimens of test series 4A were tested for strength of bond in tension. The bricks were apparently weakened by freezing and thawing to a degree such that their strength in tension was not much greater than that of the mortar. The percentage failure in the brick when the specimen broke in tension was estimated as carefully as possible for each of the 12 specimens of a group and the averages of these percentages are recorded in column 6 of table 12. In specimens made with brick no. 4, not subjected to freezing and thawing and tested for bond strength, the bricks were almost invariably stronger in tension than mortar XRa.

The data (table 12) show that best results were obtained with bricks having a suction from 12 to 40 g per minute. The average bond strength values do not differ to the extent characteristic of the 3 months strength of bond data (fig. 12) and this fact may indicate that factors other than early bond strength affect the bond durability. The individual variations (maximum and minimum values, table 12) were somewhat greater than would be predicted from the plotted data of figure 16 where specimens not subjected to durability tests are considered. This indicates partial or complete destruction of bond by alternate freezing and thawing.

No bond failures occurred in test series 1B (table 4). The presence of vertical joints in these specimens did not render them less resistant to freezing and thawing than the specimens without vertical joints.

It is difficult to devise a freezing and thawing test that may be generally considered as paralleling exposures of walls. The tests described herein were probably unduly severe insofar as those mortars

which gain strength relatively slowly are concerned and fair to the mortars of outstanding hydraulic properties. It is a well-known fact that mortars of many of the natural cements require many years for the development of any large percentage of their ultimate strength. The same is true for lime and rich in lime mortars. In buildings, many cycles of freezing and thawing of the water within the masonry are completed far more slowly than is the case in such laboratory tests and hence in practice, there is far less likelihood of damage to the mortar prior to its attainment of higher strength with consequent increased resistance to weathering than obtains in the laboratory tests. Furthermore, the procedure, thawing specimens under water, has no parallel in conditions obtaining in walls generally, and is likely only indicative of what may be expected of masonry below grade and in a severe climate. A satisfactory weathering test is at the best a moot subject and this fact should be borne in mind in reviewing the data here presented.

(c) THE TRANSVERSE STRENGTH OF BRICK BEAMS

The results of the flexure tests with specimens of test series 1C and 2C (table 4) are presented in table 13.

TABLE 13.—*Transverse tests of brick beams (5 bricks, single tier, 4 intervening mortar joints)*

[Values are averages of 3 tests]

Mortar	Modulus of rupture, brick number—											
	1 (set wet)		2 (set wet)		3 (set dry)		4 (set wet)		5 (set dry)		6 (set wet)	
	3 months	1 year	3 months	1 year	3 months	1 year	3 months	1 year	3 months	1 year	3 months	1 year
	Lb/in.²	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*	*Lb/in.²*
AI	[1] 52.0	[1] 115.2	208.0	[1] 119.8	[1] 39.4	166.4	100.7	144.8	[1] 18.2	[1] 89.1	[1] 0.0	[1] 123.7
XTd	[1] 19.7	130.6	[1] 132.3	171.1	[1] 38.8	215.4	126.0	[1] 128.2	[1] 4.1	166.7	[1] 149.2	[1] 155.3
XRa	56.6	93.9	66.8	49.5	73.5	158.5	90.5	92.9	15.8	147.0	104.7	150.3
XVa	42.9	95.5	47.6	70.0	68.2	179.2	88.8	81.2	6.8	38.8	122.9	148.3
XVb	45.1	82.0	42.0	46.9	39.9	157.9	83.4	106.0	10.4	48.6	88.7	95.0
XRc	29.8	45.0	24.2	21.2	30.4	57.2	35.0	35.5	15.2	43.9	42.1	46.8
CI	[2] 0	20.6	[2] 0	26.6	[2] 0	[2] 0	[2] 0	13.0	[2] 0	20.2	[2] 0	6.4
CII	28.5	43.9	32.2	63.2	39.3	19.6	26.8	7.4	13.0	35.2	32.9	51.2
CIII	[2] 0	27.7	[2] 0	28.0	[2] 0	11.2	[2] 0	14.4	[2] 0	9.0	[2] 0	19.5
CIV	[2] 0	29.3	[2] 0	31.3	[2] 0	10.2	[2] 0	13.5	[2] 0	[2] 0	[2] 0	20.3
BI	[1] 8.1	59.8	39.5	36.8	13.5	20.3	47.1	77.6	[1] 2.1	23.3	[1] 1.0	40.6
BIII	[1] 19.9	65.5	42.1	83.4	[1] 33.2	[1] 36.5	34.4	47.0	[1] 3.2	20.9	[1] 18.2	48.8
BIV	[1] 0	[1] 0	66.8	110.2	[1] 36.6	97.6	[1] 7.1	[1] 1.9	[1] 3.2	80.7	[1] 1.0	[1] 8
BVI	40.8	60.5	36.2	60.2	68.5	129.1	61.9	82.2	21.1	81.5	68.4	129.1
BXI	[1] 2.9	17.8	11.9	18.6	14.8	19.1	16.1	30.5	[1] .6	18.2	18.3	16.7
Average	23.1	59.2	50.0	62.5	33.1	84.7	47.9	58.4	7.4	54.9	43.2	70.2

[1] Poor extent of bond obtained with at least one of the test specimens.
[2] All 3 beams failed prior to the time of testing, extent of bond good, failure in the mortar.

The most concordant results (table 13) were obtained with mortars XRa, XVa, XVb, XRc, B III, and B VI and with bricks 1, 2, 3, 4, and 6. These mortars were of low (B III), intermediate (XRa and XVa), and high (XVb, XRc, and B VI) water retaining capacities. Where low values were obtained with mortars A I, XTd, and B IV (high strength and low water-retaining capacity), 1 or more of the 3 beams failed prior to the time of test. Mortars A I, XTd, and B IV had low shrinkage during early hardening, and high volume changes subsequent to hardening. Failure in such cases was at the juncture of brick and mortar joint and on inspection it was seen that only portions of the bonding areas of the bricks had been bonded

initially. When there is such a poor extent of bond it may be possible that volume changes in the mortar may break it. It is difficult to account for such instances of failure on any other basis.

The poor extent of bond was likely caused by the fact that the mortars of low water-retaining capacity tend to lose water on standing. This was not due to suction, as in making the beams all bricks having any appreciable suction were first wetted. The water in the mortars of low water-retaining capacities tended to separate out from the solid material while it remained on a brick and prior to pressing down the next higher brick of the test specimen. The time taken to put bricks in place was longer in the case of the 5-brick beams than it was in making the 2-brick mortar specimen. In the latter case there was not time for the mortars to lose water before the top brick was placed.

Inspection of broken specimens showed clean areas on the bottoms of upper bricks corresponding to depressed areas on the mortar beds where water had collected when the beam was made. In this connection "water-carrying capacity" has been discussed in a previous publication [31] and it was observed that the mortars of low water-retaining capacity had also usually low water-carrying capacity.

Failure was for the most part in the mortar itself in the case of mortars XRa, XVa, XVb, XRc, and B VI. In these instances separation of water from solid on standing did not occur and the bond between brick and mortar was stronger than the mortar, both at 3 months and a year. This was true also for the straight lime-sand mortars, but in this case it was impossible to move the specimens from one storage to another during the early aging period without causing failures in the mortar.

Mortar B III was to some extent unique in that it exhibited low water-retaining capacity on a porous base and yet had relatively less tendency to lose water by segregation when on an impervious base than the other mortars of low water-retaining capacity. Mortar B III was characterized by low-volume changes subsequent to hardening (see fig. 2). Failure with this mortar was usually at the juncture of brick and mortar, as was also the case with mortars B I and B XI, both highly stearated and of high water-retaining capacity. It is believed that the quantities of water-repellent materials in mortars B I and B XI may have been excessive and that at the time of making the specimens, this prevented the desirable degree of contact between the cementing material and the brick surface.

Brick no. 5 was semivitrified and smoother than most side-cut bricks, and there were more failures at the juncture of brick and mortar with this brick than with any of the other five.

(d) COMPRESSIVE STRENGTH OF BRICK PIERS

Those 3-brick portions of the beams that remained intact when the beams were broken were tested for compressive strength. Typical results are given in figure 17 where the compressive strengths of piers a year old are plotted against the compressive strengths of the six makes of brick. Mortars B XI, XRa, and A I were representative of the mortars of low, intermediate, and high compressive strengths, respectively. The data for the other mortars fall on curves of approximately the shape of those shown and lie for the most part between the curves for mortars B XI and A I.

[31] See footnote 8.

The plotted data, figure 17, show that the compressive strength of the piers increased relatively more with increased compressive strength of brick where mortar of high compressive strength (AI) was used than was the case when the mortars were of low (BXI) or intermediate (XRa) compressive strength. To get the fullest effect of brick strength on pier strength it would be necessary to use a mortar of relatively high compressive strength. At the same time the results obtained with relatively weak mortars, such as BXI, were not markedly different from mortars of intermediate strength (XRa). The terms low, intermediate, and high as here used are merely relative and refer only to the mortars described herein.

In testing the three brick piers in compression it was observed that all mortars except AI and XTd crumbled prior to failure of the piers. The approximate loads to which the mortar cracked and fell away

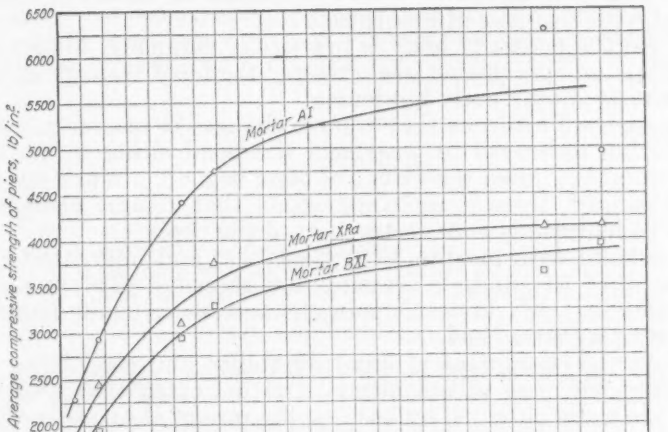

FIGURE 17.—*Compressive strength of brick piers as related to the compressive strength of bricks.*

at the edges of the joints were recorded. The ration of the load at which mortar apparently failed to the load at which the pier failed varied from approximately one-third with the weakest mortars (straight lime-sand mortars) to unity with mortars AI and XTd. With mortars of intermediate strength (XRa, XVa, BIV, etc.) the ratio often closely approximated unity, but was usually between three-fourths and four-fifths.

IV. SUMMARY AND CONCLUSIONS

It must not be considered that the results of this study are final and the following conclusions are applicable only to the conditions, materials, proportions, and types of specimens described.

1. The extent of bond was affected by the properties of both mortars and bricks, but chiefly by the water-retaining capacities of the mortars and the absorption rates of the bricks.

2. With bricks of high rates of absorption set dry, the extent and in most cases the strength of bond was best with mortars of high water-retaining capacity.

3. Although the extent of bond was good (practically complete), the strength of bond obtained with very impervious bricks (no. 5) having smooth, glassy, bonding surfaces was generally lower than that obtained with the other makes of bricks.

4. Rough surfaced bricks with low rates of absorption, and mechanically smooth and porous bricks made practically nonabsorptive by soaking in water gave good extent of bond when time in brick laying was not permitted for the water in mortars of low water-retaining capacity to separate out. When such time was allowed, the extent of bond was poor [32] with the mortars of low water-retaining capacity.

5. The maximum bond strength at 3 months was obtained in the case of all mortars with bricks having a rate of absorption of approximately 20 g of water per 30 sq in. of brick surface per minute when partially immersed (flatside down) to a depth of one-eighth inch in water. This does not imply that the maximum extent of bond was obtained with this rate of absorption.

6. When the extent of bond is practically complete, the results do not indicate an appreciable weakening of the bond through shrinkage of the mortar during early hardening.

7. There is no evidence that volume changes in mortar subsequent to hardening destroyed or weakened the bond either in vertical or horizontal joints, when the extent of bond is good. When the extent of bond is poor, there is some indication that volume changes subsequent to hardening were destructive to the bond.

8. The bond with mortars of low sorption and high strength was most resistant to alternate freezing and thawing. In the study of bond durability only impervious bricks and bricks made nonabsorptive by wetting were used.

9. From the standpoint of bond durability and considering all of the mortars included in this study, it is indicated that best results may be generally obtained by keeping the rate of absorption of bricks below the value, 40 g of water, as obtained by partial immersion (flatside down) for 1 minute in water.

10. The maximum bond strength at 3 months with the 15 different mortars increased with the compressive strength of the mortars as determined at 3 months, the conditions of curing the brick mortar specimens and the mortar cubes being the same, provided that the extent of bond was good.

11. With bricks of low rates of absorption and porous bricks made practically nonabsorptive by wetting, the highest bond strength was obtained with mortars of highest strength, when the extent of bond was good.

12. The data indicate that mortars of widely different compositions may have similar properties.

13. The data further indicate that a poor extent of bond may be obtained with certain combinations of bricks and mortars simply because the two materials are not well suited to one another and not because of any defect that would be apparent from tests according to present-day specifications.

WASHINGTON, March 14, 1934.

[32] Less than 90 percent of the bonding area.

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HEAT OF HYDRATION OF PORTLAND CEMENT PASTES

By Wm. Lerch and R. H. Bogue

ABSTRACT

When water is added to portland cement, heat is liberated, the rate and amount being a function of the composition of the cement. The heats of complete hydration have been determined of the four major compounds of portland cement, $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$. By the use of these values, and determinations of the heat of hydration which has occurred at any age, the percentage of the total available heat that has been liberated at that age may be computed. Two methods are described for use in obtaining the heats of hydration; one for ages up to 48 hours and the other for any age of paste greater than 1 day.

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I. INTRODUCTION

When water is mixed with portland cement, reactions take place as a result of which heat is evolved. Under usual conditions of concrete construction, the heat is dissipated rapidly by radiation and temperature changes within the structure are but slight and probably of little consequence. But in concrete structures of very large mass, the heat is not readily radiated and, especially under hot climatic conditions, the mass of the concrete may attain high temperatures. These temperature rises cause expansion while the cement is hardening, and may result in contractions and cracking when the eventual cooling to the surrounding temperature takes place.

Again, during construction in cold weather, special care must be exercised in the placing of concrete to insure that the grout does not freeze. Since the reactions of hydration evolve heat, they are capable of producing a degree of autoprotection against an outside temperature which might otherwise cause freezing or an inhibition of the hardening process.

For each of the above conditions of construction it is desirable that information be available on the total quantity of heat which

may be evolved from the cement and especially on the rate at which this heat is liberated. The present investigation was undertaken to determine the influence of the cement constitution, surface area and temperature on the quantity and rate of heat evolution from cements.

It appears that the processes occurring in portland cement pastes which affect the quantity and rate of heat evolution may be divided into two major classes: the heat liberated (or absorbed) by solution of the anhydrous materials, and the heat liberated (or absorbed) by the precipitation of hydrates from solution. The problem is simplified, however, since, algebraically, the heat of solution of the anhydrous materials, plus the heat of precipitation of the hydrates, is equal to the heat of hydration. The term "hydration" as herein used is the more general expression which includes whatever of hydrolysis may have occurred in any particular case. The precipitation of hydrates cannot lag appreciably behind the solution of anyhydrous materials, since the compounds involved are but slightly soluble. Hence the net heat evolved at any given age following the set of the paste is due almost entirely to the hydration which has taken place up to the time of test.

The materials selected for study included the major cement compounds (1)[1], tricalcium silicate, beta dicalcium silicate, tricalcium aluminate, and tetracalcium alumino ferrite, a number of laboratory cements prepared from commercial raw materials and burned in an experimental rotary kiln to give clinkers of systematically varying compositions, a number of commercial cements, and several definite particle size fractions obtained from one of the commercial cements.

II. PREPARATION OF THE CEMENT AND CEMENT COMPOUNDS

The cement compounds used in this investigation were prepared from chemically pure oxides and burned in an up-draft, gas-fired kiln in the manner described in a previous report (2).

The laboratory clinkers [2] were prepared from commercial raw materials burned in an 8-foot, gas-fired rotary kiln. The temperatures used in making these cements were the minimum temperatures required to obtain complete, or nearly complete, combination as determined by free lime tests (3). Gypsum was added to the cement clinkers to give 1.8 percent SO_3 and the cements were ground in a laboratory pebble mill to such fineness that 87.5 ± 0.5 percent passed the no. 200 sieve.

The commercial clinkers were obtained from the manufacturers. One of these was ground in a laboratory mill to the desired fineness and several particle size fractions separated from the ground clinker by air elutriation. Cements for test purposes [3] were made from the clinker fractions and the clinker as ground by the addition of 2.5 percent of gypsum. The clinker and gypsum were placed together in a small pebble mill with a very light charge of flint pebbles and the mill rotated for 15 minutes to accomplish intimate mixing.

[1] Figures in parentheses here and throughout the text and tables refer to the references at the end of the paper, p. 664.

[2] These clinkers and cements were prepared by W. C. Taylor, of the Portland Cement Association Fellowship.

[3] Obtained through the courtesy of R. Wilson, conservation engineer of the Portland Cement Association.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

Two methods were used to determine the heat of hydration of cement pastes: 1, the heat of hydration was calculated from the differences in the heats of solution, in a suitable solvent, of the hydrated and unhydrated cement pastes, and 2, the heat of hydration was measured directly.

1. APPARATUS AND PROCEDURE FOR HEATS OF SOLUTION

The calorimeter used for measuring the heats of solution was designed by R. S. Jessup and P. Rapp in 1925 to measure the heat of hardening of cement pastes and was later modified by W. Lerch and F. C. Hornibrook for heats of solution. The water jacket of the calorimeter, of 2,500-ml capacity, was constructed of nickel-plated brass. The jacket contained a well 13 cm deep and 10 cm in diameter to receive the calorimeter vessel and was provided with a cover 2 cm thick connected to the jacket in a manner that provided circulation of water from the jacket reservoir through the cover. Circulation of the water was effected by a motor-driven rotary stirrer made of brass. A nicrome-wire coil, of 15 ohms resistance, connected through a variable resistance to a 220-volt alternating-current line, provided the means of heating the water in the calorimeter jacket.

The calorimeter vessel was a cylindrical brass vessel of 500-ml capacity, plated with gold and provided with a bakelite cover 1.5 cm thick containing a groove 0.5 cm deep fitting snugly over the rim of the vessel. The air space between the calorimeter vessel and its containing well in the water jacket was 1 cm in width. The stirring of the liquid in the calorimeter vessel was effected by a motor-driven rotary stirrer. The shaft of the stirrer was so constructed that it made an airtight joint where it passed through the brass tube in the cover of the calorimeter jacket, eliminating diffusion of air between the calorimeter and its environment.

The calorimeter was operated adiabatically and observations of the temperature differential between the liquid in the calorimeter vessel and the water in the surrounding jacket were made by means of a five-junction copper-constantan differential thermoelement connected to a Leeds and Northrup galvanometer with scale. The thermoelement junctions were placed in a 0.5-cm glass tube, sealed at one end, the tubes then filled with paraffin, one tube immersed in the liquid of the calorimeter vessel and the other tube in the water reservoir of the jacket. When the jacket temperature became too low, as indicated by the reading on the galvanometer scale, heat could be supplied by means of the heating coil in the jacket. If the jacket temperature became too high, cold water could be added to the jacket to bring about the necessary temperature drop.

Temperature measurements of the liquid in the calorimeter vessel were made by the use of a calibrated five-junction copper-constantan thermoelement junction connected to a galvanometer and a type K Leeds and Northrup potentiometer. The thermoelement junctions were placed in glass tubes in the manner previously described, one tube being immersed in the liquid in the calorimeter vessel, the other

tube being immersed in an ice bath. It was estimated that the differential temperature readings taken in this manner are correct to 0.005° C over the range required.

The stirrer, glass-tube containers, and the heating coil immersed in the liquid in the calorimeter vessel were coated with a cellulose lacquer to protect them from attack by the solution. For the acid solutions used in this investigation, the lacquer provided an excellent protection.

The heat capacity of the calorimeter, with the vessel containing 350 g of solution, was determined with electrical energy. The amount of electrical energy input in any given experiment was computed from the time, which was measured with 0.2-second stop watch, the resistance of the constantan-wire heating coil, which was 20.04 ohms, and the current flowing through the heating coil, which was determined by measuring the potential drop across a standard 1-ohm coil in series with the heating coil.

The heat-capacity experiments were carried out in the following manner: The apparatus was assembled, the stirrers set in operation, and the temperature of the calorimeter vessel and the jacket adjusted to the same initial value of 25 ± 0.5° C. After equilibrium was established, observations of the calorimeter temperature were made in a 15-minute "fore" period. In the 15-minute calorimetric "reaction" period, electrical energy was supplied for about 5 minutes, allowing 10 minutes for equilibrium to be established. And finally observations of the calorimeter temperature were made in a 15-minute "after" period. The corrected calorimetric temperature rise was taken as equal to the observed rise in temperature of the calorimeter from the beginning to the end of the reaction period less the average of the temperature changes which occurred in the fore and after rating periods.

A similar procedure was followed in the heat of solution experiments, with the electrical energy being replaced by the energy evolved on dissolving the cement in the solution. In the calorimetric reaction period, the calibrated thermoelement was removed from position and replaced by a funnel through which the cement, whose temperature was 25.0 ± 0.5° C, was added at a more or less uniform rate for about 5 minutes. Then the funnel, the end of which extended to about 1 cm above the surface of the solution, was removed and the thermoelement replaced. In the heat of solution experiments 3 g of cement, calculated on the water-free basis, were used. The amount of solution was 350 g less that amount of water which would be added in the cement.

The electrical energy supplied for the determination of the heat capacity was approximately 2,400 cal which gave a temperature rise of about 7° C. The heat of solution obtained from the cements and hydrated materials varied from 1,450 to 2,200 cal and the temperature rise varied in these experiments from 4.2 to 6.3° C.

A preliminary investigation of the solubility of portland cement and the cement compounds indicated the necessity of using different acid solutions for dissolving these several materials. The solvents selected for the solution of the cement compounds, the cements, and their hydration products were: For tricalcium aluminate, a two-normal nitric acid solution; for tetracalcium alumino ferrite, a two-normal

hydrochloric acid solution; and for the calcium silicates and cements, a solution of two-normal nitric and 0.25 normal hydrofluoric acids. With these solvents complete solution was attained in each case.

2. APPARATUS AND PROCEDURE FOR DIRECT HYDRATION

The calorimeter used for measuring the heats of hydration directly was that employed by P. Rapp and C. H. Jumper (4) for measuring the changes in temperature of cement pastes during setting and adopted by W. Lerch and R. Briant for determining heat of hydration. The procedure in the present experiments was as follows: The cement and water were thoroughly mixed in a small tin can, copper-constantan thermoelements inserted in the paste and the can placed in a double-walled vacuum flask which was tightly stoppered with a cork stopper. The thermoelements were connected to a recording potentiometer which recorded the temperature of the cement paste at 15-minute intervals.

During the experiments described in this report, the apparatus was set up in a constant temperature room at $21 \pm 1°C$ ($70 \pm 2°$ F), and all materials were brought to room temperature before starting an experiment. The water was placed in the tin can, the cement was then added and thoroughly mixed with the water by a mechanical stirrer. The stirring was continued for 1 minute to insure complete and homogeneous mixing of the paste. Three thermoelement junctions were inserted and distributed through the mass of the paste in order to obtain a representative average temperature.

From the data obtained in this manner, the heat evolved by the cement from the beginning of the reaction to any given time can be calculated. The total heat evolved at any given time is equal to the heat absorbed by the calorimeter and contents plus the heat lost by radiation to the surroundings. For this calculation, it is necessary to know the heat capacity and the initial and final temperatures of the calorimeter and contents, and the rate of loss of heat by radiation from the calorimeter.

The heat capacity of the calorimeter was taken as equal to that of the inner wall of the vacuum flask (computed from its mass and specific heat) plus the heat capacity of the tin can, plus the heat capacity of the cement paste (calculated as 0.2 and 1.0 cal per degree for the cement (5) and water, respectively). The radiation-loss constant was determined for each vacuum flask by observing the rate of cooling of a definite quantity of hot water in the tin can placed in the flask.

In each experiment 200 g of cement and 67 g of water were used.

For periods of time longer than 48 hours, this method is not practicable because of the small temperature difference which then exists between the calorimeter and its surroundings.

A number of determinations were made with two commercial cements to determine the reproducibility of the results by this method. In 16 experiments (8 each on 2 cements) the average deviations from the mean values were ± 3.2 and 3.0 percent—or ± 1.8 and 2.0 cal per g, respectively. The total heats per gram were 57 and 68 cal, 46 and 55 of which were computed from radiation and 11 and 13 from the temperature rise of the calorimeter.

IV. HEAT EVOLVED ON COMPLETE HYDRATION

The ultimate quantity of heat that can be liberated by a cement, in the absence of secondary reactions, is that quantity which is evolved on the complete hydration of the constituent compounds to the equilibrium condition imposed by the conditions of the test. A knowledge of the heats of complete hydration of the cement compounds permits the computation of the percentage of the total available heat that has been evolved at any age of test. Accordingly, the heats of complete hydration of the cement compounds and of a number of clinkers were determined.

In the preparation of the hydrated materials, the respective compounds and cement clinkers were ground to an impalpable powder and water was added in sufficient quantity to produce a paste of approximately normal consistency (6). The pastes were thoroughly mixed and placed in an Erlenmeyer flask which was then tightly stoppered and sealed with paraffin wax. These pastes were allowed to hydrate at room temperature for about 1 month. At that time the flasks were broken away from the hardened pastes, the latter were reground and mixed with sufficient additional water to again give a plastic paste. These mixtures were allowed to continue their hydration as before. The hardened pastes were reground twice at subsequent intervals and treated in a similar manner. After this treatment microscopic and X-ray examination of the hydrated compounds failed to reveal the presence of the unhydrated compounds, except in the case of beta dicalcium silicate which still contained a small amount of unhydrated material, estimated to be about 2 or 3 percent. Reexaminations of the hydrated compounds at later ages have shown no appreciable changes in the heat values obtained as described and reported below.

It should be pointed out that the term "complete hydration" as used in this investigation refers to a limiting condition of hydrolysis and hydration which the cement compounds in mortars and concretes may be expected to approach but never to exceed. It is for this reason that the values were obtained under conditions of water concentration similar to those encountered in mortars and concretes rather than in an excess of water. Hence the values given may not in all cases denote the theoretical equilibrium condition. As an example, it may be mentioned that the composition of the calcium silicate in equilibrium with saturated calcium hydroxide was found to be $3CaO.2SiO_2.nH_2O$. But in mortars the hydrolysis has not been found to proceed appreciably beyond the composition $2CaO.SiO_2.nH_2O$. Hence the values given for the "complete hydration" of $3CaO.SiO_2$ and $2CaO.SiO_2$ represent the heats liberated on conversion to $2CaO.SiO_2.nH_2O$ rather than to the hypothetical equilibrium composition of $3CaO.2SiO_2.nH_2O$.

The results obtained from this phase of the investigation are given in table 1. The data presented in the table include the composition of the materials examined, the heat of solution of the anhydrous materials, the heat of solution of the hydrated materials on the ignited basis, the heat evolved on complete hydration, obtained by the difference between these two and, in the case of the cement clinkers, the calculated heat of hydration computed from the compound composition of each clinker.

TABLE 1.—*Heat evolved on complete hydration of cement compounds and portland cement clinkers*

	Partial analyses of cement compounds and of cement clinkers						Computed compound composition of cement clinkers						Heat anhydrous materials	Hydrated materials on ignited basis	Heat evolved on complete hydration	Calculated heat of hydration	Difference between experimental and calculated values
	CaO	Al_2O_3	Fe_2O_3	SiO_2	MgO	B_2O_3	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO					
Pure compounds																	
													cal/g	*cal/g*	*cal/g*	*cal/g*	*Percent*
C_3A	62.3	37.9	0.05	0.01					100				733	526	207		
C_4AF	46.3	20.8	33.0	.03						100			519	419	100		
C_3S	73.8	.1	.06	25.8			100						632	512	120		
βC_2S	65.1	.1	.06	34.4		0.4		100					563	501	62		
CaO (7)													828.9	550.3	278.6		
MgO (8)													862	659	203		
Clinkers, series K-3																	
No. 4	63.7	4.0	4.9	23.9	3.1		44	36	2	15	3.1	0	623	526	97	100	+3.1
No. 5	64.7	7.0	2.0	22.1	3.7		46	29	15	6	3.7	0	649	523	126	118	−4.8
No. 15	66.6	7.4	1.7	19.8	4.0		62	10	17	5	4.0	1.5	666	521	145	133	−8.3
No. 17	65.4	5.4	5.5	20.0	3.3		69	5	5	17	3.3	0	638	519	119	120	+0.8

It is shown that the heats of complete hydration of the cement compounds, as obtained in this study, are as follows:

Tricalcium aluminate	cal/g	207
Tetracalcium alumino ferrite	do	100
Tricalcium silicate	do	120
Beta dicalcium silicate	do	62

Four determinations were made on each compound. The probable error of the determination is computed to be ±3 cal per g.

The values given for lime (7) (278.6 cal per g) and magnesia (8) (203 cal per g) were available in the literature and were not redetermined in this investigation.

The heat of hydration of $3CaO.Al_2O_3$ to $3CaO.Al_2O_3.6H_2O$ has been reported by Thorvaldson (7) as 214.3 cal per g. Considering the difficulties involved in preparing these compounds in pure form, this value is in good agreement with results obtained in the present investigation.

The values obtained for the complete hydration of the cement clinkers shown in table 1 are in fair agreement with the values for complete hydration computed from the compound composition of the clinkers. The values obtained for the heat of solution of the anhydrous and hydrated clinkers are larger than the values which would be obtained from calculations using the heat of solution of the several compounds as given in the table. This is probably due to the use of different solvents in determining the heat of solution of the several cement compounds. However, the heats of hydration of the clinkers when calculated by this method are identical with the calculated values obtained from the heat of hydration factors of the individual compounds. The percentage differences between the experimental and the computed values are shown to range from +3.1 to −8.3, the experimental value being taken as the basis of comparison. It

cannot be stated at this time if these divergencies are due solely to experimental error or if they involve some inherent characteristics of the cement clinkers whereby the latter differ slightly from the cement compounds when prepared separately. However, these differences are relatively small.

The generally satisfactory agreement between experimental and computed heats of complete hydration leads to the belief that secondary reactions, if they occur on the hydration of clinkers, are relatively insignificant so far as heat transfer is concerned and that the total heat available on the hydration of a clinker may be computed with a fair degree of precision from the heats of hydration of the constituent compounds.

The only essential difference in composition between a clinker and a cement is the presence of calcium sulfate in the latter. This is usually added to the clinker in the form of gypsum ($CaSO_4.2H_2O$) but, during the grinding process, the gypsum may have been partially or completely dehydrated to plaster ($CaSO_4.\frac{1}{2}H_2O$) or soluble anhydrite ($CaSO_4$), respectively. The calcium sulfate has been found to react with tricalcium aluminate hydrate during set or early hardening to form calcium sulfoaluminate ($3CaO.Al_2O_3.3CaSO_4.31H_2O$). In computing the total heat available from the hydration of a cement it is accordingly necessary to consider the heat involved in the hydration of the plaster or anhydrite and the heat involved in the reaction of the hydrated gypsum with the hydrated tricalcium aluminate to form calcium sulfoaluminate. For the reactions

$$CaSO_4.\frac{1}{2}H_2O\ (c) + 1\frac{1}{2}\ H_2O\ (l) = CaSO_4.2H_2O\ (c) \text{ and}$$

$$CaSO_4\ (c, \text{soluble anhydrate}) + 2H_2O\ (l) = CaSO_4.2H_2O\ (c)$$

the heats evolved are, respectively, 3.7 and 2.7 kcal per mol, (9) or 46 and 34 cal per g SO_3. With the usual percentages of calcium sulfate in cement, this represents a heat value of about 1 cal per g of cement. Inasmuch as the extent of dehydration of the gypsum during grinding is a variable and indeterminate quantity and the heat involved is slight, it appears best to avoid the introduction of a heat factor for the calcium sulfate hydration in the computations of total available heat from cements.

The heat liberated by the reaction

$$3CaO.Al_2O_3.6H_2O(c) + 3CaSO_4.2H_2O(c) + 19H_2O(l) = 3CaO.Al_2O_3.3CaSO_4.31H_2O(c)$$

was computed to be about 149 cal per g of SO_3. This calculation was made from data obtained in the present investigation on the heats of solution of $3CaO.Al_2O_3.6H_2O(c)$ and $3CaO.Al_2O_3.3CaSO_4.31H_2O(c)$ in aqueous HCl and from the data on $CaSO_4.2H_2O(c)$ given in the International Critical Tables. Since the foregoing reaction has been found generally to occur during the setting process or shortly thereafter, and the value is significant, it appears proper to take it into consideration in the computations of total heat available on the complete hydration of cements. This has been done in the computations appearing in tables 2 and 3 referred to later in the paper.

V. THE RATE OF HEAT EVOLUTION AT EARLY AGES BY THE DIRECT HYDRATION METHOD

A large number of cements have been examined by the direct hydration method to determine the quantity of heat evolved at ages up to 48 hours. By this method it was possible to calculate the heat evolved at hourly intervals. Some of these results are presented in the accompanying figures which show the values obtained during the first 24 hours.

The materials examined in this part of the investigation included 61 laboratory cements prepared from commercial raw materials to give clinkers of systematically varying composition and 10 commercial

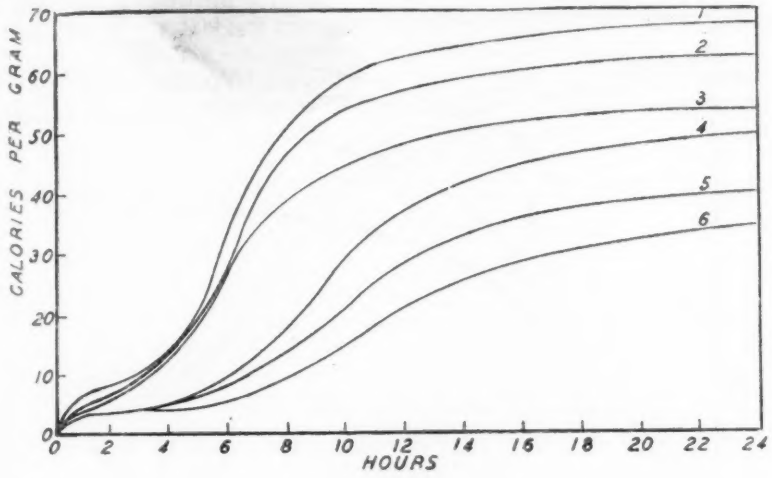

FIGURE 1.—*Heat evolution from cements in which* $3CaO.Al_2O_3$ *and* $4CaO.Al_2O_3.Fe_2O_3$ *are the major variables.*

No.	C_3S	C_2S	C_3A	C_4AF	C_3F	MgO	Free CaO
1	43	30	18	4	0	2.8	1.4
2	47	26	16	7	0	3.0	.3
3	43	33	11	10	0	3.1	.3
4	43	34	7	13	0	3.1	0
5	39	40	2	16	0	3.1	.1
6	41	39	0	14	3	3.0	0

clinkers. Gypsum was added to give 1.8 percent SO_3 and the materials ground to such fineness that 87.5 ± 0.5 percent passed the no. 200 sieve.

In the case of the laboratory cements, the raw materials were proportioned with the intent of varying certain compounds in the clinker and maintaining the other compounds constant. The clinkers were analyzed, including the free lime determination, and the compounds computed. Although the final computations showed that compositions were not precisely as designed, the nature of the effects of composition on rate of heat liberation is clearly indicated.

The results obtained on cements wherein the tricalcium aluminate was decreased by substituting ferric oxide for alumina are shown in figure 1. These results indicate that each decrease in the tricalcium aluminate content is accompanied by a decrease in the quantity of heat liberated during the first 24 hours. (In the figures and tables

abbreviations in the formulas of the compounds have been used as follows: $C_3S = 3CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $C_3A = 3CaO.Al_2O_3$; $C_4AF = 4CaO.Al_2O_3.Fe_2O_3$.)

Figure 2 shows the effect of decreasing the tricalcium silicate and increasing the dicalcium silicate with all other factors substantially constant. These results indicate that each decrease in the tricalcium silicate content is accompanied by a decrease in the quantity of heat liberated during the first 24 hours, with the exception of cement no. 57. This cement contained 2.1 percent free lime, a compound which hydrates rapidly and liberates a large quantity of heat per unit weight.

The results obtained with cements in which the magnesia content is varied are shown in figure 3. In these cements the tricalcium

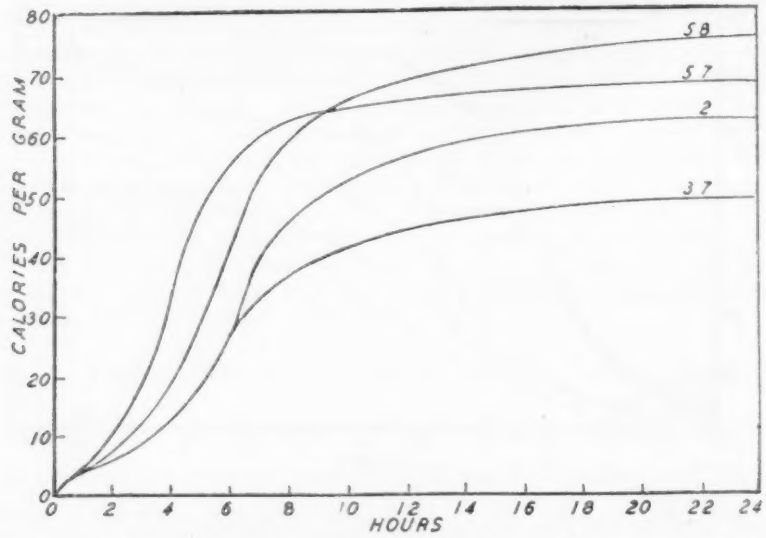

FIGURE 2.—*Heat evolution from cements in which* $3CaO.SiO_2$ *and* $2CaO.SiO_2$ *are the major variables.*

No.	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO
58	62	13	14	7	3.3	0.7
57	45	28	15	7	2.9	2.1
2	47	28	16	7	3.0	.3
37	16	58	16	6	3.0	.2

aluminate and tetracalcium alumino ferrite were maintained constant and the calcium oxide and silica were adjusted to maintain a substantially constant tricalcium silicate content. Thus, the dicalcium silicate decreased as the magnesia increased. Varying the magnesia content in this manner results in only slight differences in the quantity of heat liberated at 24 hours and the results show no definite trend with relation to the magnesia content.

The heat data from three commercial cements which were ground in a laboratory mill to 3 degrees of fineness have shown that the rate with which the heat is liberated increases with increased fineness. The data on one of these cements are plotted in figure 4. The other two cements gave similar results. It is observed that the reaction occurs earlier with the finer cements but that, at 24 hours, the total amount of heat evolved is not greatly different for the different

degrees of grinding. At 48 hours the differences became even smaller.

Still other factors which have been found to contribute to the differences in the rate of heat evolution at very early ages are the temperature of the paste during hydration, the water/cement ratio and the quantity of retarder present. The effects of these factors, however, become small after 48 hours.

The curves presented in this report, showing the heat evolved at various time intervals, are of interest in a consideration of the processes occurring during the setting and hardening of the cement. In general, the curves contain four distinct phases. There is an initial rise in the temperature with all compositions, which occurs during the

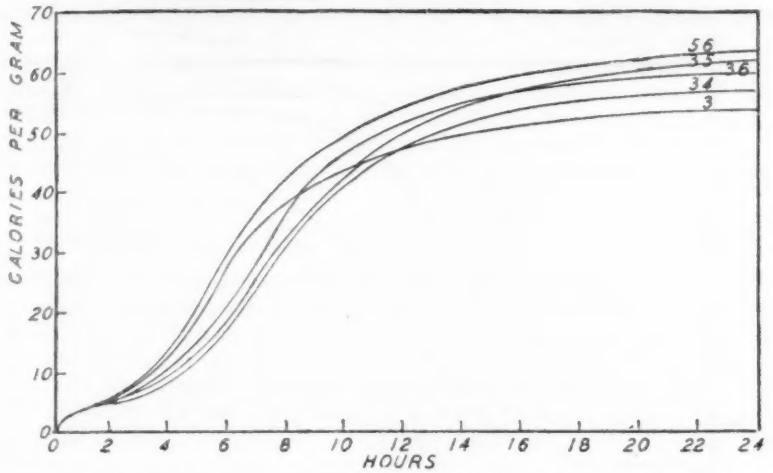

FIGURE 3.—*Heat evolution from cements in which* MgO *and* $2CaO.SiO_2$ *are the major variables.*

No.	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO
56	47	23	11	9	9.9	0.1
35	41	33	11	9	4.9	.2
36	42	30	11	9	7.0	.3
34	41	36	11	9	1.4	.2
3	43	33	11	10	3.1	.3

first few minutes. This is followed by a period in which there are only slight thermal changes; the duration of this period varies from a few minutes to several hours depending on the composition of the cement. In the third phase there is a rapid evolution of heat followed by the fourth phase wherein the thermal changes become relatively slow.

The initial rise appears to be due to the heat of wetting, the mechanical heat of stirring, and probably in part to the heat of solution. This is indicated by the observation that the maximum temperature of this period has been reached in the first few minutes, that is, by the time the first temperature reading is recorded.

The next period, in which there is a very slow evolution of heat, is a period in which it appears that the water is becoming saturated with the various compounds of the cement. The rate of solution is then dependent on the relative solubility of the various compositions used, on the fineness of the cement, and on the temperature of the paste during this period.

The period of rapid evolution of heat appears to be a period of rapid solution of anhydrous material and precipitation of hydrated material. The algebraic sum of these processes for the compounds of cement is, at this stage, highly exothermic. It has been observed that the beginning of this period of rapid evolution of heat occurs at about the same time period as that at which the initial set takes place (4). The layer of hydrated crystals and amorphous hydrated material, deposited around the unhydrated portion of the grains, as also the depletion of the solvent, tend to retard the further penetration of water and hydration of the cement. This results in a diminution in the rate of evolution of heat in the succeeding periods, even though the hydration has not approached completion in that time.

A number of observations support these postulations. A microscopic study of the process of hydration of tricalcium aluminate and

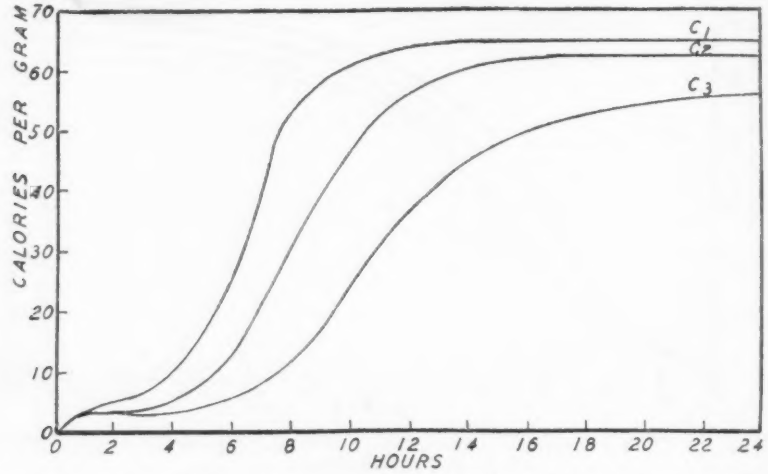

FIGURE 4.—*Heat evolution from a cement ground to different degrees of fineness.*

No.	Percent passing no. 200 sieve
C_1	96
C_2	89
C_3	83

tetracalcium alumino ferrite gives evidence of the formation within a few minutes of crystals of a hydrated phase. This would lead to the conclusion that these materials dissolve rapidly which is in agreement with the nature of the data obtained with those materials. The microscopic examination of hydrating tricalcium silicate indicates that several hours are required for the first crystals of calcium hydroxide to appear and for the first evidence of colloidal hydrate formation. The experiments with beta dicalcium silicate show no evidence of this period of rapid evolution of heat.

Hence, changes in composition of the cement whereby the more soluble compounds are diminished may be expected to prolong the period of quiescence which precedes the rapid rise in temperature. That condition is especially noticeable in the cements in which the tricalcium aluminate is decreased, and is noticeable to a lesser degree in cements in which tricalcium silicate is decreased. Likewise, in accordance with the above theory, acceleration of the reactions by the

physical methods of finer grinding of the cements and higher initial temperature is found to advance the period of rapid heat evolution.

All of the heat data obtained on the laboratory cements at 48 hours were subjected to a mathematical analysis by the method of least squares. As a result of this analysis it became apparent that the heat liberated by the hydration of the free CaO could not be observed when the percentage of free CaO present was not greater than about 0.5 percent. The heat liberated by CaO on complete hydration at 20 C was found by Thorvaldson, Brown, and Peaker (7) to be 278.6 cal/g. Thus, the presence of 0.5 percent free CaO in clinker would, on complete hydration, contribute 1.4 cal/g of clinker at 20 C (68 F), which is less than the probable error of the method. Also, the magnesia was found to be without appreciable effect at 48 hours and the effect of the dicalcium silicate could not be evaluated because of the very small amount of heat evolved by that compound at early ages.

A solution of the normal equations, in which tricalcium aluminate, tricalcium silicate, and tetracalcium alumino ferrite were assumed to be responsible for all of the heat evolved at 48 hours, produced the following values, representing the heats of hydration at 48 hours contributed by each percent of the above compounds per gram of cement:

Tricalcium aluminate	1.50
Tricalcium silicate	1.00
Tetracalcium alumino ferrite	.40

Inasmuch as cement compositions are often reported only in terms of the oxide components, it may sometimes be desirable to interpret the heat data in terms of the oxides. Since the percentages of the compounds present are a linear function of the percentages of the oxides (10) the desired transformations may readily be made. The results obtained for the contribution of each percent of the oxides in the cement to the heat evolution at 48 hours of one gram of cement are as follows:

CaO	+4.08
SiO_2	−7.61
Al_2O_3	−2.75
Fe_2O_3	−2.76

In applying these data to cements, the percentage of lime must be corrected for the lime present in the retarder as calcium sulfate.

On applying the factors given above for the cement compounds to the computation of the heat evolved at 48 hours from the 61 laboratory cements, the calculated and experimental heats were found to agree within a probable error of ±3 cal/g of cement.

Ten commercial cements of widely varying composition also were examined in a similar manner and equally satisfactory agreement was found between the computed and experimental results.

Since the rate of heat evolution, in contradistinction to the total heat of hydration, is sensibly affected by many variables, such as surface area, temperature, available water, retarder present, thermal history of the clinker, etc., in addition to the composition, the heat factors given above can be considered as applying only under the specific conditions of manufacture and test imposed upon the cements investigated. The value of the data lies in the definite effects indicated, due to changes in the composition with a given set of conditions, and under these circumstances the effect on the rate of heat evolution at early ages due to changes in the percentage of the compounds present is clearly shown.

VI. THE RATE OF HEAT EVOLUTION BY THE HEAT OF SOLUTION METHOD

Several cements were examined by the heat of solution method to determine the quantity of heat evolved at various ages after mixing the paste. For this purpose the cements were thoroughly mixed with 40 percent of water, by weight, and the pastes placed in 1-inch glass vials. The vials were immediately stoppered with corks and sealed with paraffin. The vials were then placed in constant temperature cabinets where they remained until required for the heat of solution determinations. Some of the vials were cured at 25 C (77 F), and others at 35 C (95 F), to compare the rate of evolution of heat at these different temperatures.

TABLE 2.—*Rate of evolution of heat from cements of variable composition*

Number		1	3	6	8	43S	106	Commercial clinker (c)
		Partial oxide composition						
CaO		62.7	64.2	64.9	66.6	62.6	66.6	65.7
Al_2O_3		4.0	6.9	3.9	6.8	4.1	7.4	7.0
Fe_2O_3		5.1	2.0	5.0	2.0	4.7	1.7	2.0
SiO_2		25.5	23.4	22.7	21.0	25.4	19.8	22.1
MgO		2.5	3.1	3.1	3.0	2.8	4.0	2.6
		Computed compound composition (percent)						
$3CaO.SiO_2$		27	31	57	53	27	63	51
$2CaO.SiO_2$		53	43	22	20	52	10	24
$3CaO.Al_2O_3$		2	15	2	15	3	17	15
$4CaO.Al_2O_3.Fe_2O_4$		15	6	15	6	14	5	6
MgO		2.5	3.1	3.1	3.0	2.8	4.0	2.6
Free CaO		0	.6	.1	2.3	0	1.4	
Gypsum added		3.8	3.8	3.8	3.8	3.8	3.8	2.5
		Computed heat available from complete hydration, cal/g						
		91	112	110	128	93	136	120
		Heat of hydration, neat cement						
1 day:	Cal/g obtained at 25 C	35	38	44	49			
	Cal/g obtained at 35 C					38	71	48
	Percent of total heat obtained at 35 C					41	52	40
2 days:	Cal/g obtained by direct method	45	64	74	76	42	82	
3 days:	Cal/g obtained at 25 C	49	61	54	74			
	Cal/g obtained at 35 C	51	63	61	82	50	95	67
	Cal/g computed at 35 C [1]	43	66	66	88	44	90	65
	Percent of total heat obtained at 35 C	56	56	55	64	54	70	56
7 days:	Cal/g obtained at 25 C	50	71	67	86			
	Cal/g obtained at 35 C	57	75	73	97	52	105	90
	Cal/g computed at 35 C [1]	48	73	75	98	49	101	89
	Percent of total heat obtained at 35 C	63	67	66	76	56	77	75
28 days:	Cal/g obtained at 25 C	63	82	76	106			
	Cal/g obtained at 35 C	70	93	86	113	70	117	95
	Cal/g computed at 35 C [1]	63	87	83	106	66	108	99
	Percent of total heat obtained at 35 C	77	83	78	88	75	86	79
90 days:	Cal/g obtained at 25 C	74	94	86	114			
	Cal/g obtained at 35 C	76	94	92	117	76	117	101
	Cal/g computed at 35 C [1]	71	92	90	111	71	112	104
	Percent of total heat obtained at 35 C	84	84	84	91	82	86	84
180 days:	Cal/g obtained at 35 C	75	98	93	117			106
	Cal/g computed at 35 C [1]	73	96	93	115			108
	Percent of total heat obtained at 35 C	83	88	85	91			88

[1] Computed from factors of Woods, Steinour, and Starke (reference 11).

The results obtained from seven cements are given in table 2. In addition to data on composition and gypsum additions, this table contains the data on heat evolved as obtained by the heat of solution method at ages of 1, 3, 7, 28, 90, and 180 days at temperatures of 25 and 35 C (77 and 95 F). The 2-day values obtained by the direct method also are included. Woods, Steinour, and Starke (11) have computed factors which indicate the contribution of the individual compounds to the heat evolution at ages 3, 7, 28, 90, 180, and

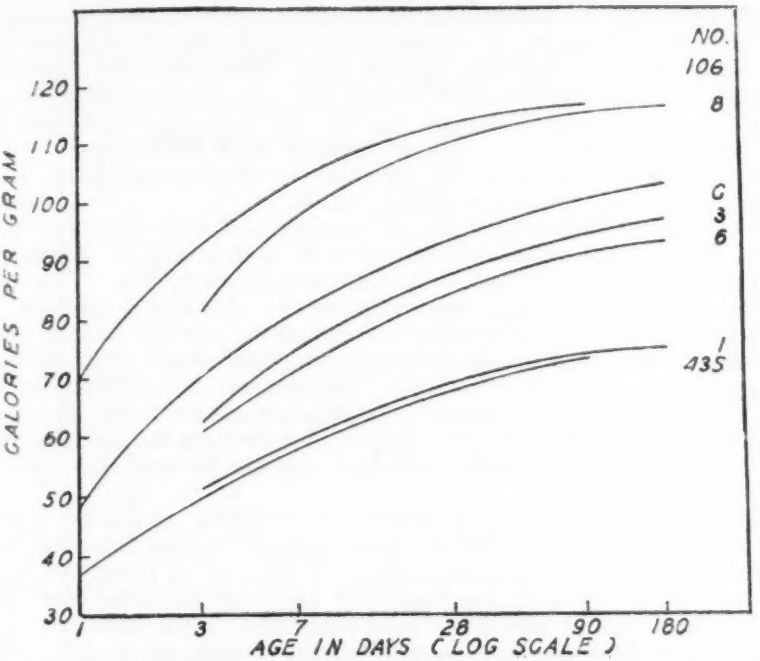

FIGURE 5.—*Heat evolution at 35 C from cements of different composition at ages to 180 days.*

No.	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO
106	63	10	17	5	4.0	1.4
8	53	20	15	6	3.0	2.3
C	51	24	15	6	2.6	—
3	31	43	15	6	3.1	.6
6	57	22	2	15	3.1	.1
1	27	53	2	15	2.5	0
43S	27	52	3	14	2.8	0

365 days. Seventeen laboratory cements of a wide range in composition were used by those investigators, these being ground to about 99.8 percent passing the 200 no. sieve. By the use of these factors, values were computed of heat liberation at corresponding ages for the cements examined. These computed values also are recorded in table 2.

The amounts of heat liberated from the above cements at the ages tested are shown in figure 5.

An examination of the results obtained from these cements confirms the earlier finding that tricalcium aluminate and tricalcium silicate are compounds which contribute large quantities of heat of hydration to the cements at all ages, while the dicalcium silicate and

tetracalcium alumino ferrite contribute lesser quantities of heat and at a slower rate. Thus cement no. 3 evolves more heat than cement no. 1, and cement no. 8 evolves more heat than cement no. 6 where the major differences in composition are an increase in the tricalcium aluminate content and a decrease in the tetracalcium alumino ferrite. Also cement no. 6 evolves more heat than cement no. 1, and cement no. 8 evolves more heat than cement no. 3, but in these pairs the major differences in composition are an increase in the tricalcium silicate content and a decrease in the dicalcium silicate content.

The number of cements used in this investigation was not sufficient for a statistical analysis to determine the heat factors for the individual compounds at the different ages of test. However, the calculated values obtained by the use of factors given by Woods, Steinour, and Starke are generally in good agreement with the experimentally obtained values at 35 C. The application of those factors, however, cannot be expected to be quantitative for the reasons given in the discussion of the direct hydration method.

The values obtained by the direct method at 2 days are in fair agreement with the extrapolated values at 35 C obtained by the heat of solution method at 1 and 3 days with one exception. This comparison is not rigid, however, because, by the direct method, the temperature during hydration is not constant, whereas in the heat of solution method, the curing temperatures of the small specimens used remain approximately constant. The general concordance of the results, however, gives assurance of the soundness of the two quite independent methods of examination and permits the extrapolation of data between the early and late periods covered by the two methods.

The amounts of heat available on complete hydration of the cements, as previously defined, have been computed from the compositions and are set down in table 2. By the use of these values, the percentage of the available heat that has been liberated from each cement at each test period has been computed. It is seen that about half of the total available heat is liberated between 1 and 3 days, about three quarters in 7 days, and from 83 to 91 percent in 6 months, when the pastes are cured at 35 C (95 F). It may also be noted that both the total quantity and the rate of heat liberation are greatest with those cements high in tricalcium aluminate and tricalcium silicate.

The amounts of heat evolved at 35 C (95 F) are consistently higher than those evolved at 25 C (77 F), but the magnitude of the difference is not large.

VII. EFFECT OF SURFACE AREA ON RATE OF HEAT EVOLUTION

Several definite particle size fractions obtained from a commercial cement by air elutriation were examined by the heat of solution method to determine the quantity of heat evolved by the different fractions at various intervals. Pastes were prepared from these fractions in the manner previously described and the pastes cured at 35 C (95 F).

The results obtained from these fractions, together with results obtained from the whole clinker as ground, are given in table 3 and

are shown graphically in figure 6. The table gives the particle size of each fraction, expressed both in microns and in terms of the surface area of each fraction in sq cm/g; the oxide composition and the computed compound composition of each clinker fraction; the amount of gypsum added; the calculated heat available from the complete hydration of the cements; the experimentally obtained values of the heat evolved at various intervals; and the values obtained at the various intervals calculated to percent of the total heat available.

This study did not include all of the fractions separated from this cement, but the number examined covers a wide range of particle size

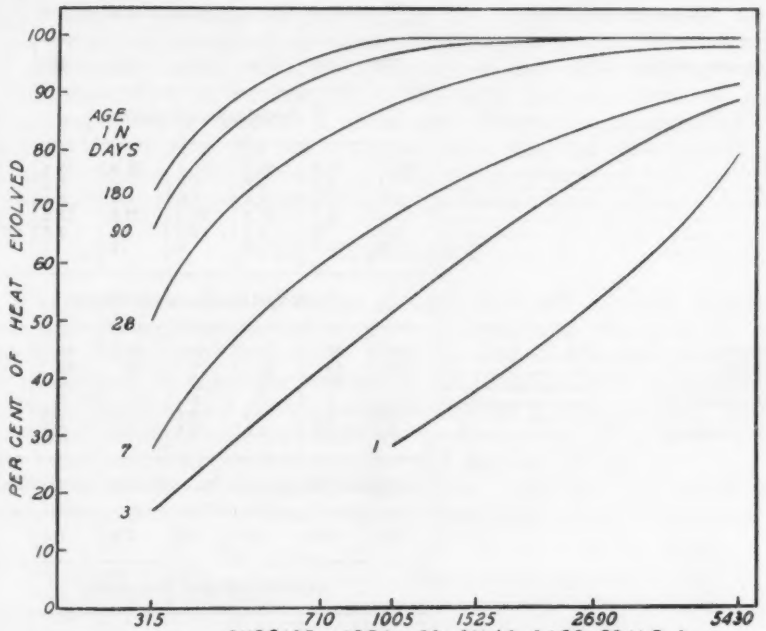

FIGURE 6.—*Percentage of total heat evolved from differently sized fractions of a cement at ages to 180 days.*

and surface area and was considered sufficient to indicate the effect of particle size on rate of evolution of heat from this cement.

The computed compound composition of the fractions is shown not to be identical, the most pronounced difference being a consistent variation in the calcium silicates present. The tricalcium silicate content decreases and the dicalcium silicate content increases as the particle size increases. This is in agreement with results previously reported by Carlson and Bates (12). These changes in compound composition bring about a progressive decrease, as the particle size increases, in the computed quantity of heat available upon complete hydration.

The results given in table 3 and figure 6 show a pronounced difference in rate of evolution of heat from the variously sized fractions as indicated by the experimentally obtained values, expressed in cal/g; and also as indicated by the computed values showing the percent of the total available heat that has been evolved at each age. Thus,

the 0 to 5 micron fraction had evolved 87 percent of its total heat in 3 days, whereas the 48 to 60 micron fraction had evolved only 17 percent of its heat at that age. At 28 days the fine fraction was almost completely hydrated whereas at that time the coarse fraction was but 50 percent hydrated. The intermediate fractions evolved heat at rates which corresponded to their respective surface areas.

TABLE 3.—*Rate of evolution of heat from a commercial cement and from several definite particle size fractions obtained from the cement*

Particle size in microns		Less than 5	5 to 10	10 to 16	16 to 20	20 to 30	48 to 60	Whole cement
Surface area, sq cm/g [1]		5,430	2,690	1,525	1,005	710	315	1,675
		Partial oxide composition						
CaO		66.2	66.2	66.2	66.1	65.9	65.1	65.7
Al_2O_3		7.2	6.8	6.5	6.8	7.0	7.4	7.0
Fe_2O_3		2.0	2.0	1.8	1.9	1.9	2.1	2.0
SiO_2		21.3	21.7	22.3	22.4	22.3	22.3	22.1
MgO		2.6	2.5	2.4	2.4	2.4	2.6	2.6
SO_3		.3	.2	.2	.2	.2	.2	.2
		Computed compound composition						
$3CaO.SiO_2$		58	57	55	52	50	45	51
$2CaO.SiO_2$		16	18	21	24	25	29	24
$3CaO.Al_2O_3$		16	15	14	15	15	16	15
$4CaO.Al_2O_3Fe_2O_3$		6	6	6	6	6	6	6
MgO		2.6	2.5	2.4	2.4	2.4	2.6	2.6
Gypsum added		2.5	2.5	2.5	2.5	2.5	2.5	2.5
		Computed heat available from complete hydration, cal/g						
		126	123	120	120	118	117	120
		Heat of hydration, neat cement						
1 day:	Cal/g obtained at 35 C	99	64	44	37	----	----	48
	Percent of total heat liberated	79	52	37	31	----	----	40
3 days:	Cal/g obtained at 35 C	109	88	74	61	47	20	67
	Percent of total heat liberated	87	72	62	51	40	17	56
7 days:	Cal/g obtained at 35 C	113	100	85	83	69	31	90
	Percent of total heat liberated	90	81	71	69	58	27	75
28 days:	Cal/g obtained at 35 C	120	104	107	101	101	58	95
	Percent of total heat liberated	95	85	89	84	86	50	79
90 days:	Cal/g obtained at 35 C	126	120	115	114	109	76	101
	Percent of total heat liberated	100	98	96	95	93	65	84
180 days:	Cal/g obtained at 35 C	124	120	118	118	112	84	106
	Percent of total heat liberated	99	98	99	99	95	72	88

[1] Based on calculation from microscopic determinations of diameters.

A small part of the differences in rate of heat evolution may be accounted for by the differences in composition with respect to the calcium silicates. Tricalcium silicate, which is present in the greatest amount in the finer fractions, hydrates more rapidly than dicalcium silicate. This would tend to accelerate the hydration of the finer fractions. However, the differences in heat liberated due to the slight variations in composition appear to be of minor significance in

these separate fractions as compared with the large differences shown to be due to the particle size. This is indicated by the differences obtained for the computed values of the heat available from complete hydration of the several fractions. These variations are relatively small compared to the divergencies in the experimentally obtained values, at early ages, for these various fractions.

It should be pointed out that large differences were observed in the surface areas of the several fractions as computed from microscopic determination of the mean particle sizes. The surface areas varied from 315 sq cm/g in the 48 to 60 micron fraction to 5430 sq cm/g in the minus 5 micron fraction. This explains the large differences in rate of heat evolution obtained on these fractions as compared with the small differences observed after 24 hours of the differently ground cements described in section V. Although surface areas of the cements reported in section V were not determined, a number of tests have shown that the surface areas that may be anticipated by grinding a clinker (in a laboratory mill) to finenesses of 87.5 and 97 percent passing the no. 200 sieve range from about 1,800 to 2,500 sq cm/g.

VIII. SUMMARY

1. The partial and total heats of hydration of portland cement pastes have been determined by two independent methods: 1, by measuring the heat of hydration directly, and 2, by measuring the heats of solution in the same solvent of the hydrated and unhydrated samples. The first, or direct method, utilizes a vacuum flask calorimeter and is applicable for ages up to 48 hours. The second, or indirect method, is applicable for ages of 1 day and longer.

2. The total heats available upon the complete hydration of compounds present in portland cement were found to be as follows:

	cal/g
Tricalcium silicate	120
Beta dicalcium silicate	62
Tricalcium aluminate	207
Tetracalcium alumino ferrite	100

In addition, the following values were taken from the literature:

Magnesia	203
Free CaO	279

The heat of hydration of the calcium sulfate in portland cement, which may have been partially or completely dehydrated during the grinding process, is shown to be inappreciable. The heat of reaction of gypsum and tricalcium aluminate hydrate to form calcium sulfoaluminate is found to be 149 cal/g of SO_3.

3. By use of the above heat values, the total heat available on the complete hydration of a clinker or cement may be computed from the composition. Experimental values obtained on a number of clinkers were found to be in good agreement with computed values of heat of complete hydration.

4. By use of the computed values representing heat of complete hydration of a cement, together with heat of solution tests of the original cement and of the paste at any desired age, the percentage of the total available heat that has been liberated at any age of test may be computed. Such computations have shown that a relatively large proportion of the total available heat is liberated in a few days but

that the heat may continue to be evolved at a progressively decreasing rate through the later ages.

5. Factors have been computed which indicate the amount of heat contributed by the compounds $3CaO.Al_2O_3$, $3CaO.SiO_2$, and $4CaO.Al_2O_3.Fe_2O_3$ to the total heat liberated during the first 48-hour period after mixing with water. These factors may not be applied rigidly to commercial cements because of indeterminate variables in the latter which affect the rate of heat evolution at early ages, but they may be used under specified conditions of manufacture and test to predict the effect of changes in composition on the rate of heat evolution at early ages.

6. The rate of heat evolution is found to increase as the surface of the cement is increased. With the laboratory-ground cements, herein described, varying in surface area from about 1,800 to 2,500 sq cm/g, differences in fineness resulted in differences in rate of heat evolution during the first few hours after mixing the paste but approached equivalent values in 1 or 2 days. A period of many months may be required, however, to bring about an hydration of a coarse fraction equivalent to that brought about in a finer fraction in a few days.

7. The amounts of heat evolved at 35 C are consistently higher than those evolved at 25 C, but the magnitude of the differences is not large.

IX. REFERENCES

1. Bogue, Ind. Eng. Chem., anal. ed., vol. 1, p. 192, 1929.
2. Lerch and Bogue, Jour. Phys. Chem., vol. 31, p. 1627, 1927.
3. Lerch and Bogue, Ind. Eng. Chem., Anal. ed., vol. 2, p. 296, 1930.
4. Rapp and Jumper, Jour. Am. Concrete Inst., vol. 1, p. 28, 1929.
5. Hartman, Zement, vol. 3, p. 57, 1927; Rock Products, vol. 30, no. 5, p. 74, 1927.
6. Cf. Standard Specifications for Portland Cement, Am. Soc. Testing Materials. Federal Specifications for Portland Cement, 55–C–191.
7. Thorvaldson, Brown, and Peaker, Jour. Am. Chem. Soc., vol. 51, p. 2678, 1929; vol. 52, p. 80, 910, 1930.
8. Roth and Chall, Z. Electrochem., vol. 34, p. 185, 1928.
9. International Critical Tables, vol. V, p. 196.
10. Dahl, Rock Products, vol. 32, no. 23, p. 28, 1929.
11. Woods, Steinour, and Starke, Ind. Eng. Chem., vol. 24, p. 1207, 1932; Eng. News Record, Apr. 6, 1933.
12. Carlson and Bates, Rock Products, vol. 25, no. 21, p. 18, 1932.

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